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Melamine-Based Porous Organic Polymers Supported Pd(II)-Catalyzed Addition of Arylboronic Acids to Aromatic Aldehydes

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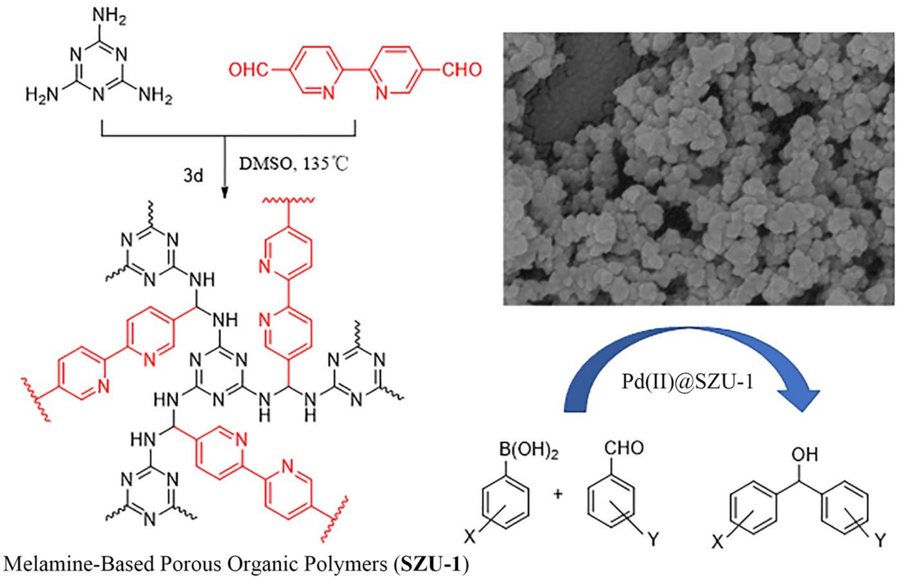
Abstract

A new type melamine-based porous organic polymers (**SZU-1**) has been synthesized with melamine and 2,2′-bipyridyl-5,5′-dialdehyde by a one-pot method and fully characterized. Divalent palladium salts were coordinated to this polymer network which successfully catalyzed the nucleophilic addition reaction of arylboronic acids to aromatic aldehydes. With only 1.0 mol% heterogeneous catalyst loading, high reaction yields (> 85%) can be achieved in most cases. The scope of substrates was also investigated and the catalyst showed universal applicability.

Graphic Abstract

The loose and porous melamine-based porous organic polymers (**SZU-1**) are synthesized by melamine and 2,2′-bipyridyl-5,5′-dialdehyde. The performance of **SZU-1** was characterized and most of the substrates achieved high yield (> 85%) in the catalytic performance test.



Keywords Palladium catalysis · Heterogeneous catalysis · Porous organic polymers

1 Introduction

Microporous materials have received great attention for their extremely high surface area and surface functional groups diversities, and a great progress has been made in the past 2

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10562-020-03508-1.

Extended author information available on the last page of the article decades [1–4]. Materials such as zeolite, silica, and activated carbon (pore size < 2 nm) have been widely used as catalysts and catalyst supports [5]. However, their applications in heterogeneous catalysis still remain undeveloped [6–8]. The covalently bonded porous organic polymers (POPs) have the following advantages: (1) POPs have a high functional groups diversity and can be coordinated with different catalysts [9]; (2) compared with other homogeneous catalysts, POPs are insoluble in any solvent, so the catalyst can be easily recycled [10]; (3) their wettability can be easily adjusted, which is very beneficial for improving mass transfer and catalyst performance [11]; (4) a large number of nanopores can effectively enrich the reactants and accelerate the reaction rate [12]. In summary, POPs-based catalysts are much more recyclable compared to homogeneous catalysts. In some reactions, even the same catalyst activity as in homogeneous reactions can be achieved [13].

Over the past decade, our group has been working on Pd(II)/2,2′-bipyridine-catalyzed nucleophilic addition reactions. A series of different nucleophilic addition reactions, including the addition of arylboronic acids to aromatic aldehydes [14], imines [15] and α, β-unsaturated carbonyl compounds [16] have been developed, in which highly efficient additions were achieved under mild conditions. Based on our previous research, we want to further expand its application on heterocatalysis. The addition reaction of arylboronic acids to aromatic aldehydes will be tested under heterogeneous catalytic conditions to probe the reusability of the precious palladium catalysts. Though porous materials like zeolites are currently widely used as heterogeneous supported catalysts [17, 18], it is difficult to coordinate them with transition metals due to the limitation of its elemental structure because most transition metals need to be coordinated with organic ligands to achieve good catalytic activity [19–22]. So, the application of inorganic porous materials in diverse organic functional groups transformations is greatly limited.

Therefore, heterogeneous catalytic materials that can effectively coordinate with metals are highly expected. In 2009, Schwab et al. synthesized a nitrogen-rich polymer network (SNW-1) [23] with a high surface area, in which melamine and 1,4-phthalaldehyde were used as raw materials in a one-pot process. Melamine is a very simple and readily available compound, and the method does not require anhydrous and oxygen-free conditions, which is very suitable for large-scale synthesis. The authors tried a variety of different monomers, confirming that this method is highly selective, making the functionalization of target materials possible. SNW-1 has a very high surface area (> 1000 m^2/g) and excellent heat resistance ($T_{dec} > 400$ °C), which demonstrated high potential as a catalyst supporting material. In our research, 4,4′-biphenyldicarboxaldehyde was used as the monomer and the bipyridine ligand can be easily implanted into the POPs to effectively coordinate with palladium (Scheme 1). The produced POPs (**SZU-1**) is loose and porous, which is an ideal support for heterogeneous catalysts.

SZU-1 with bipyridine segments has been successfully synthesized, and its ^{13}C NMR spectrum and FT-IR were proved to be consistent with the reported similar structure in literature [23]. BET test showed that surface area is high to 333 m^2/g.

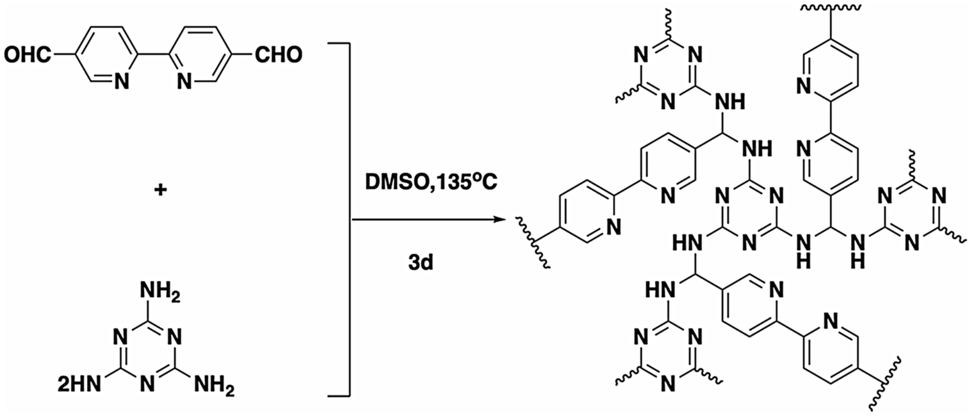
Initially, $Pd(OAc)_2$ was selected as the catalyst to coordinate with **SZU-1**, but only a trace amount of product is given in the addition of arylboronic acids to aromatic aldehydes. Then the more active cationic Pd(II) becomes a better choice. Under cationic Pd(II) conditions, good yields had been achieved and functional group tolerance is perfect. At the same time, the recycle test of the catalyst showed that the yield can still be higher than 80% after 4 cycles.

2 Experiment

2.1 Catalyst Preparation

2.1.1 Preparation of SZU-1 (bipyridine/biphenyl = 1:2)

Melamine (101 mg, 0.80 mmol), [2,2′-bipyridine]-5,5′-dicarbaldehyde (86 mg, 0.40 mmol) and



Scheme 1 Synthesis of **SZU-1**

[1,1′-biphenyl]-4,4′-dicarbaldehyde (168 mg, 0.80 mmol) were mixed and completely dissolved in DMSO (5 mL) at 100 °C. 2 mL of 3.0 M aqueous acetic acid was added. All the mixture was loaded in a hydrothermal reactor and sealed. The reaction was running at 135 °C for 72 h. Cooled the reactor to room temperature and a gel-like product was obtained. THF (15 mL) was added and stirred for 12 h, then centrifuged at 10,000 rpm for 5 min to separate the solid yellow powder, which was finally vacuum dried at 120 °C for 12 h. The yield was 83%.

2.1.2 Preparation of $PdCl_2$@SZU-1

40 mg of SZU-1 and 50 mg of $PdCl_2$ were mixed in 10 mL of CH_3CN, refluxed for 12 h, filtered and dried under vacuum. The color of SZU-1 changed from light yellow to orange after coordination. The coordination rate is 5.2 wt% calculated by the mass change after ashing.

2.2 Catalyst Characterization

Brunauer–Emmett–Teller (BET) test is at TriStar II 3020 (Micromeritics., US), 120 °C degassing for 24 h. X-ray diffraction (XRD) was tested on X'Pert-Pro MPD (PANalytical B.V., Netherlands). The Solid-state NMR spectrum was recorded by AVANCEIII/WB-400 AVANCEIII/WB-400 Solid-state NMR spectrometer wide bore (Bruker Corporation, Germany). ^{1}H NMR spectra were recorded on a BRUKER AVANCE III HD (400 MHz) spectrometer. ^{13}C NMR spectra were recorded on a BBRUKER-OLD AVANCEIII HD-400 (100 MHz) spectrometer with complete proton decoupling. Fourier transform infrared (FT-IR) spectra were collected from Nicolet 6700 spectrometer (Nicolet Instrument Corp., US) with a wavenumber range of 4000–400 cm^{-1}.

2.3 Catalyst Testing

$PdCl_2$@SZU-1 (10 mg, 1.0 mol%) and $AgNO_3$ (5 mg, 2.0 mol%) were mixed in CH_3NO_2 (2 mL), and stirred at 80 °C for 1 h, then 1 mmol arylboronic acid and 0.5 mmol aromatic aldehyde added. The reaction was carried out for 24 h. During the reaction, an appropriate amount of arylboronic acid could be added. The reaction mixture was concentrated and the target product was purified by column chromatography on silica gel to determine the catalyst efficiency.

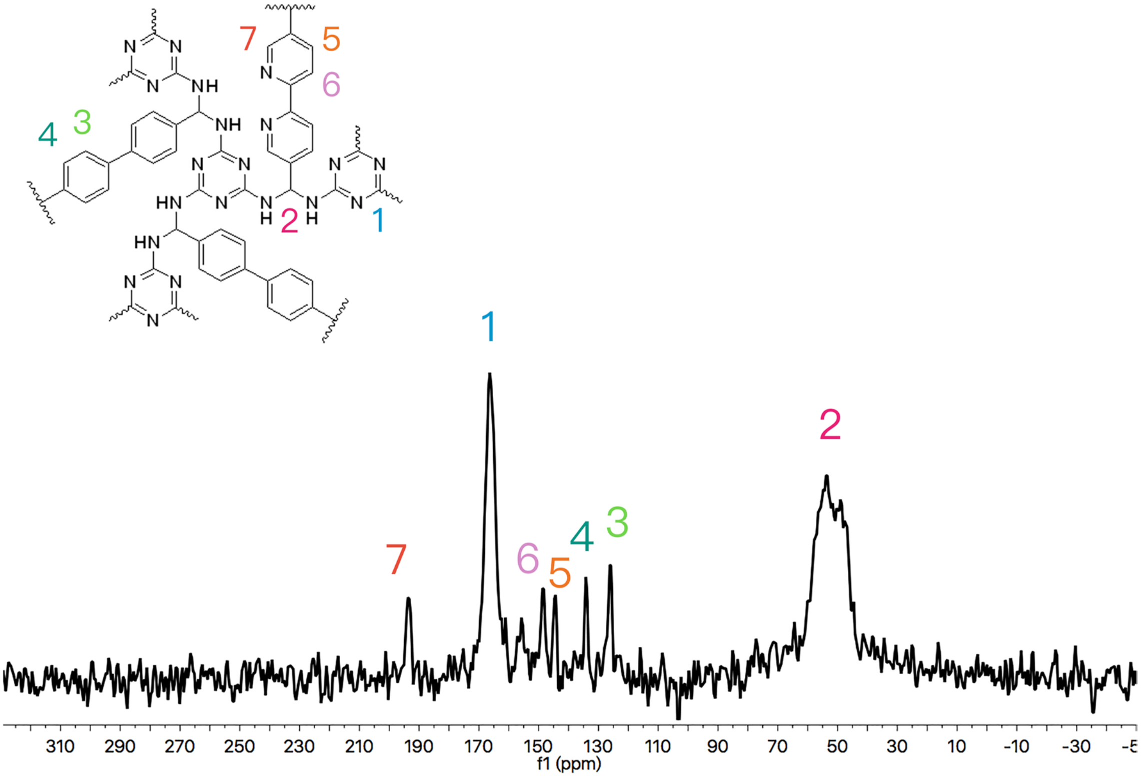


Fig. 1 ^{13}C MAS NMR spectrum of **SZU-1**

3 Results and Discussion

3.1 Catalyst Characterization

SZU-1 was firstly characterized by solid-state NMR spectrum and FT-IR (Fig. 1). The ^{13}C MAS solid-state NMR spectrum showed that two peaks at 166 ppm and 53 ppm can be assigned as the carbons on the azine ring of melamine, and -NH- in melamine is boned to –CH–, which is also consistent with the literature [23]. As **SZU-1** was composed of biphenyl and bipyridyl segments, the two peaks at 148 ppm and 144 ppm belong to the carbons at positions **3** and **4** of bipyridines. The peak of carbon atoms **6** showed up at 193 ppm. 134 ppm and 129 ppm correspond to two pairs of aromatic carbons of biphenyl.

FT-IR spectroscopy (Fig. 2) showed the melamine-NH_2 stretching vibration at 3400 cm^{-1}, and the primary ammonia deformation vibration at 1700 cm^{-1}. 1550 cm^{-1} and 1480 cm^{-1} attribute to the quadrant and semicircle stretching of the triazine rings [24]. This concluded that melamine had been successfully incorporated into the network. In addition, the stretching vibration peak (1600 cm^{-1}) of the imine bond was not observed on the FT-IR spectrum. It revealed that the imines from the condensation of melamine and aldehyde were subjected to a secondary addition.

In addition, **SZU-1**, $PdCl_2$ and **Pd@SZU-1** were characterized by X-ray diffraction (Fig. 3). The result shown in Fig. 3 revealed that $PdCl_2$ has been coordinated on **SZU-1**.

The morphology of **SZU-1** was tested by electron scanning electron microscope (SEM) and it's found that the **SZU-1** was loose and porous spherical particles (Fig. 4). The BET test results gave a surface area as 330 m^2/g and a NLDFT micropore volume as 0.67 cm^3/g (Fig. 5).

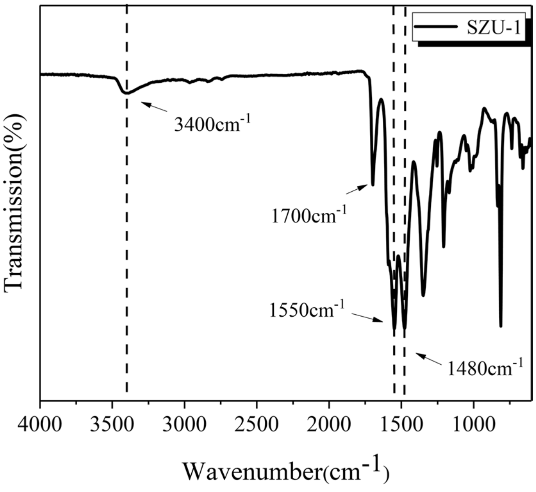


Fig. 2 FT-IR spectrum of **SZU-1**

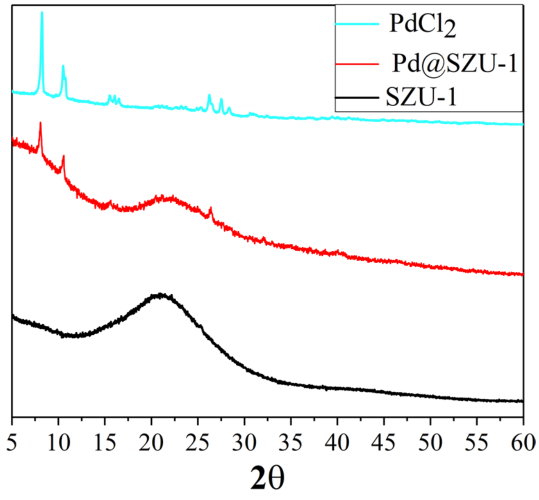


Fig. 3 X-ray diffraction (XRD) of $\mathbf{PdCl_2}$ (blue), **Pd@SZU-1** (red), **SZU-1** (black)

3.2 Catalyst Performance Evaluation

Then the catalytic performance of **SZU-1** was evaluated. Initially, as shown in Table 1, $Pd(OAc)_2$ was used as the palladium catalyst and reacted in 4 different solvents (Table 1, Entries 1–4). However, only trace amount of product was detected in nitromethane (Table 1, Entries 1). Therefore, the more reactive cationic $PdCl_2/AgNO_3$ was chosen as the palladium species. The vacant coordination sites of the cationic palladium centers make it easier for the unsaturated bonds to coordinate, which helps the following unsaturated bonds insertion. As shown in Entries 5–7, the reaction takes nitromethane as a solvent at 80 °C for 24 h (Table 1, Entry 7), and the starting materials are completely converted. Nitromethane is a very good reaction solvent for its high polarity and weak coordination ability [14]. The effect of reaction time on the reaction results was also considered, and it was found that the raw materials had almost completely been consumed in 24 h (Table 1, Entries 7–8). It was concluded that the best results were under $PdCl_2/AgNO_3$ with nitromethane as the solvent, with a yield of 95%. In addition, the catalytic activity was also tested for those catalysts with different percentages of bipyridine segments (Table 1, Entries 7, 9, 10). The result showed that the SZU-1 supported catalyst with 33%, 66%, and > 99% bipyridine had almost the same performance. Therefore, for economic considerations, an **SZU-1** with a bipyridyl percentage of 33% was used as the optimal catalyst.

Then, the scope of the substrates was investigated. Substrates are divided into two groups: *p*-nitrobenzaldehyde was fixed as the reactant to react with different arylboronic

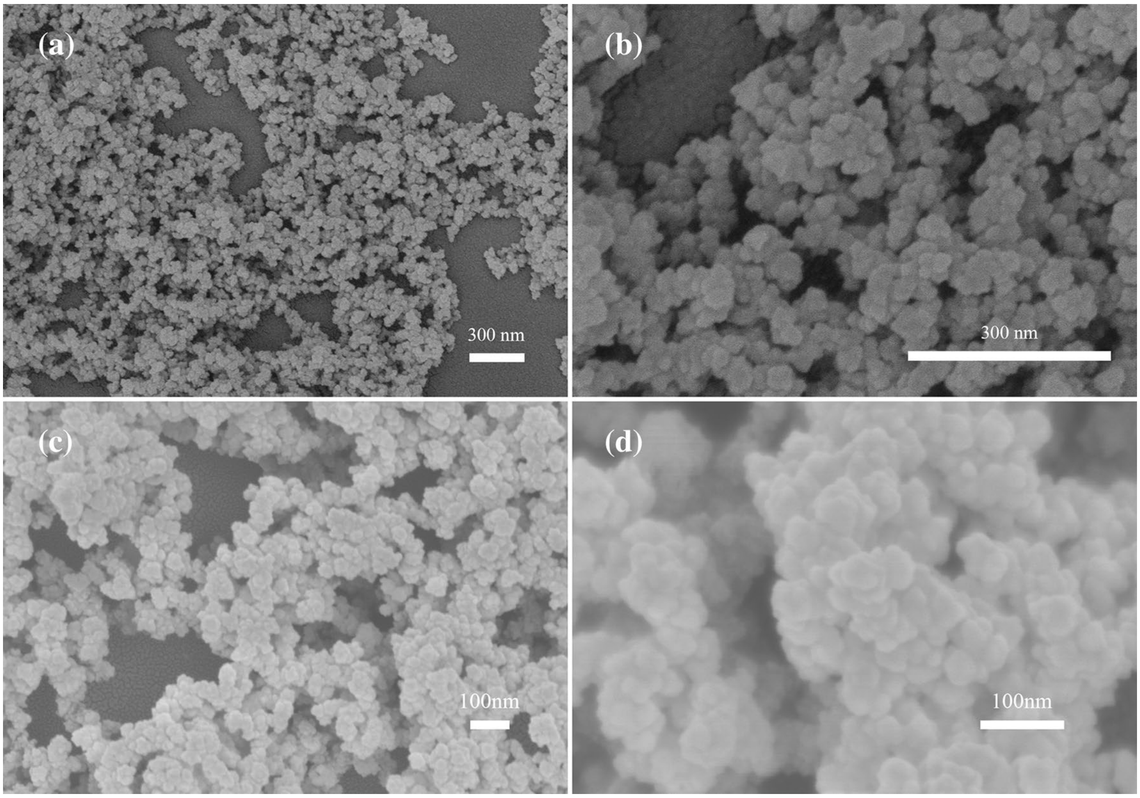


Fig. 4 Scanning electron micrograph (TEM) of **SZU-1**

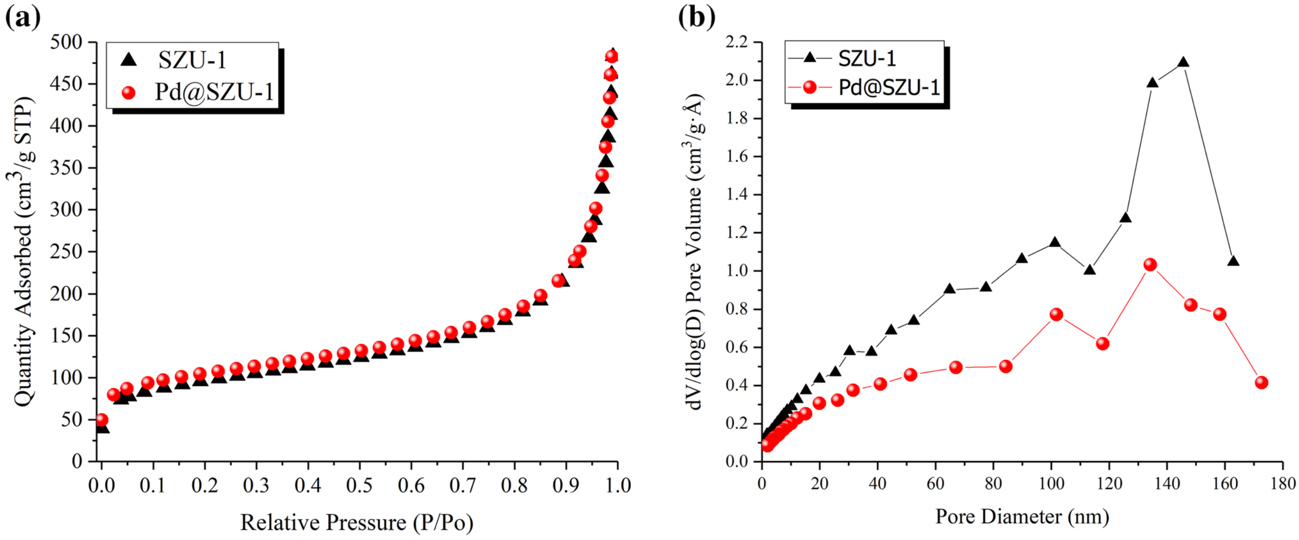
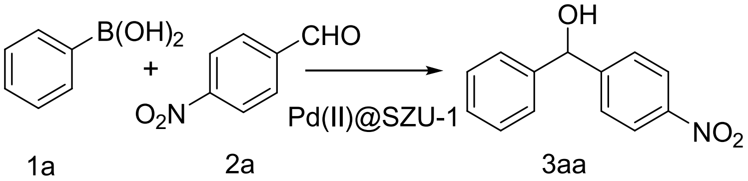


Fig. 5 Nitrogen sorption isotherms and NLDFT pore size distribution of **SZU-1** (triangle), **Pd@ SZU-1** (circle)

acids in one group, and phenylboronic acid as the fixed reactant to test aromatic aldehydes in another group. It can be concluded from Tables 1 and 2 that **SZU-1** showed very high catalytic reactivity. The similar catalytic performance as the

Table 1 Effect of phenylboronic acid addition to *p*-nitrobenzaldehyde



Entry	Catalyst	Bipyridyl percentage (%)[a]	Solvent	Time (h)	Yield (%)[b]
1	$Pd(OAc)_2$	> 99	CH_3NO_2	24	Trace
2	$Pd(OAc)_2$	> 99	THF/H_2O	24	0
3	$Pd(OAc)_2$	> 99	Toluene/H_2O	24	0
4	$Pd(OAc)_2$	> 99	CH_3OH	24	0
5	$PdCl_2/2AgNO_3$	> 99	Dioxane	24	34
6	$PdCl_2/2AgNO_3$	> 99	Toluene/H_2O	24	52
7	$PdCl_2/2AgNO_3$	> 99	CH_3NO_2	24	95
8	$PdCl_2/2AgNO_3$	> 99	CH_3NO_2	12	61
9	$PdCl_2/2AgNO_3$	33	CH_3NO_2	24	91
10	$PdCl_2/2AgNO_3$	66	CH_3NO_2	24	94

Reaction conditions: $PhB(OH)_2$ (1 mmol), 4-nitrobenzaldehyde (0.5 mmol), Pd@ SZU-1 (10 mg, 1 mol%), $AgNO_3$ (5 mg, 2.0 mol%), solvent (2 mL).

[a] Bipyridyl percentage $= \frac{\text{bipyridine}}{\text{bipyridine+biphenyl}}$

[b] Isolated yield

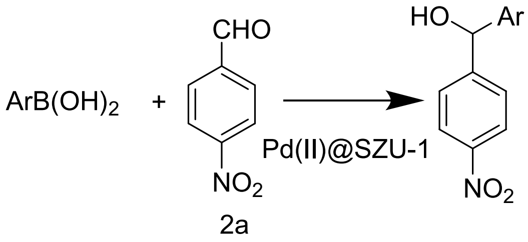
general homogeneous catalyst was achieved. Compared with our previously research, the catalytic performance is comparable to that of homogeneous reactions [14].

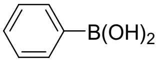
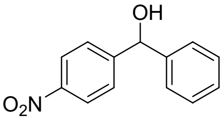
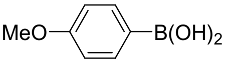
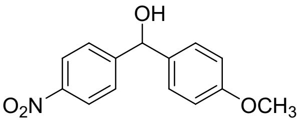
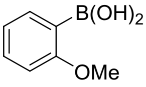
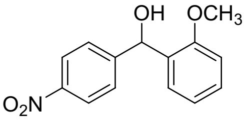
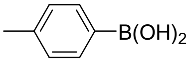
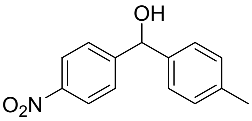
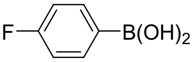
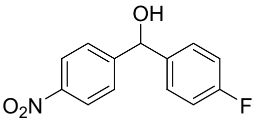
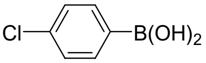
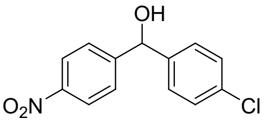
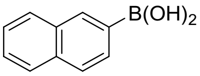
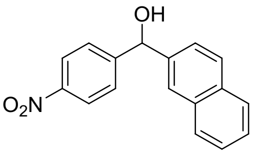
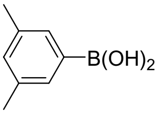
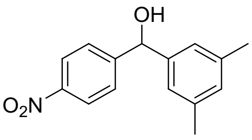
Since this reaction is a nucleophilic addition, theoretically an electron-donating group on nucleophiles and an electron-withdrawing group on electrophiles would favor the reaction. Therefore, it's observed in Table 2 that different arylboronic acids all gave excellent results with > 90% isolated yields, whether it is the strong electron-donating groups **1b**, **1c** (Table 2, Entries 2, 3), the medium electron-donating groups **1d**, **1h** (Table 2, Entries 4, 8) or the weaker electron-withdrawing groups **1e**, **1f** (Table 2, Entries 5, 6). As the arylboronic acid with an electron donating group can be decomposed by protonolysis, it is necessary to add a certain more amount of arylboronic acid in a timely manner to get a complete conversion. In addition, **1g** (Table 2, Entry 7) with a larger steric hindrance also gave a high yield. It can be concluded that the POPs-supported catalysts have good catalytic performance for different arylboronic acids.

As shown in Table 3, different aromatic aldehydes were used as substrates. When the substituents on the benzene ring changes from electron-withdrawing groups to electron-donating groups, the yield changed drastically. For example, strong electron-withdrawing groups of **2a**, **2b**, and **2c** (Table 3, Entries 1, 2, 3) not only made the aldehydes be more stable and difficult to be oxidized, but also promoted the reaction yield to more than 95%. However, with the decrease of electron-withdrawing properties, the yields also showed a downward trend. For the aldehydes with halogen substituents, the reaction yields decreased for **2d** and **2e** (Table 3, Entries 4, 5). When benzaldehyde **2f** was subjected in the reaction (Table 3, Entries 6), only a 55% yield was given due to the less electrophilicity and its unstability in the air. Finally, for **2g** and **2h** (Table 3, Entries 7, 8) with electron-donating groups, the yields were greatly reduced. Aromatic aldehydes with electron-donating groups are not only difficult to be added but they are easily oxidized to carboxylic acids during the reaction, which made the reaction yield dropped sharply.

Finally, the catalytic cycle test was also carried out and the results were shown in Fig. 6. The result revealed that after 4 complete cycles, the reaction yield still reached more than 80%, and for the first three cycles the yields were more than 90%. By the comparison of TEM images (Fig. 7), it is clearly observed that a number of Pd(0) nanoparticles (dark dots in Fig. 7b) were generated after 4 cycles. A very similar phenomena were observed in literature [25]. The formation of Pd(0) was supposed to be caused by the cross-coupling of arylboronic acids, and the addition of arylboronic acids to aldehydes is a divalent-Palladium catalysis in which Pd(0) is

Table 2 Cationic Pd(II)@SZU-1 catalyzed addition of arylboronic acid to *p*-nitrobenzaldehyde

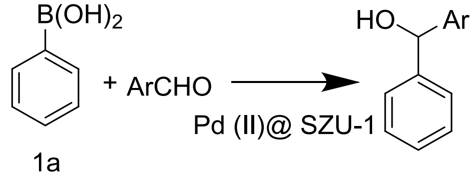


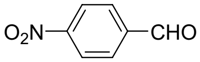
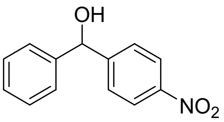
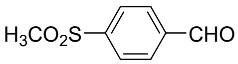
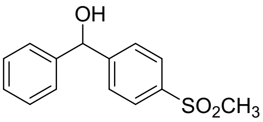
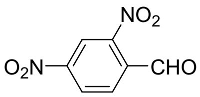
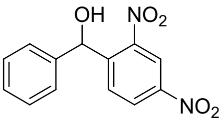
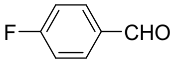
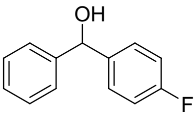
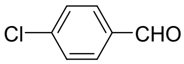
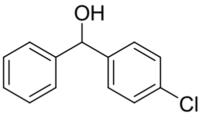
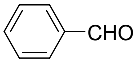
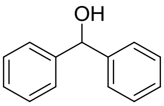
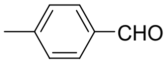
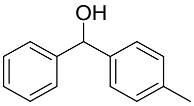
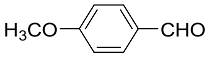
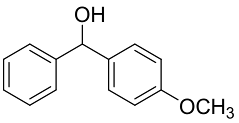
Entry	$ArB(OH)_2$		Product		Time (h)	Yield (%)[a]
1		**1a**		**3aa**	24	95
2		**1b**		**3ba**	24	81
3		**1c**		**3ca**	24	89
4		**1d**		**3da**	24	95
5		**1e**		**3ea**	24	94
6		**1f**		**3fa**	24	88
7		**1g**		**3ga**	48	71
8		**1h**		**3ha**	24	94

Reaction conditions: $ArB(OH)_2$ (1 mmol), *p*-nitrobenzaldehyde (0.50 mmol), Pd(II)@SZU-1 (10 mg, 1 mol%), $AgNO_3$ (5 mg,), CH_3NO_2 (2 mL), 80 °C.

[a] Isolated yield

Table 3 Cationic Pd(II)@SZU-1 catalyzed addition of phenylboronic acid to aromatic aldehydes



Entry	ArCHO		Product		Time (h)	Yield (%)[a]
1		**2a**		**3aa**	24	95
2		**2b**		**3ab**	18	96
3		**2c**		**3ac**	18	95
4		**2d**		**3ad**	24	60
5		**2e**		**3ae**	24	85
6		**2f**		**3af**	48	55
7		**2g**		**3ag**	48	30
8		**2h**		**3ah**	48	17

Reaction conditions: $PhB(OH)_2$ (1 mmol), ArCHO (0.50 mmol), Pd(II)@ SZU-1 (10 mg, 1 mol%), $AgNO_3$ (5 mg), CH_3NO_2 (2 mL), 80 °C

[a] Isolated yield

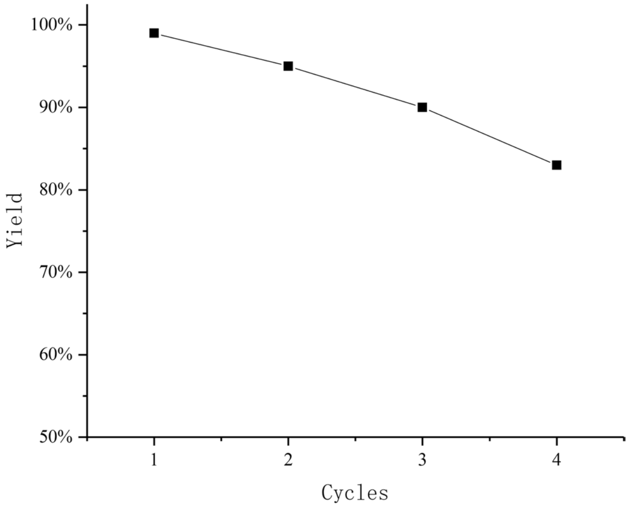


Fig. 6 **SZU-1** catalytic cycle test

non-reactive [14]. It's speculated the deactivation of Pd(II) to Pd(0) caused the yield drops in recycling experiments.

4 Conclusion

In our research, a nitrogen-rich porous organic polymers (**SZU-1**) was synthesized and characterized. It has high surface area (330 m^2/g). Its loose and porous surface with bipyridine segments is very suitable as supporting material for heterogeneous palladium catalysis. Characterization by FT-IR, XRD and ^{13}C NMR confirmed that bipyridine segments have been successfully incorporated and palladium catalyst was coordinated. In terms of catalytic performance, this heterogeneous catalyst achieved high yields for the nucleophilic addition of arylboronic acids to aldeydes under relatively mild conditions with low catalyst loadings. The reaction showed excellent tolerance to different arylboronic acids and aldehydes. Among 15 different substrates, 10 examples gave yields of over 80%, indicating the excellent catalytic efficiency and substrate tolerance of this catalyst. Moreover, SZU-1 demonstrated excellent chemical stability, and the yield can still exceed 80% after 4 catalytic cycles.

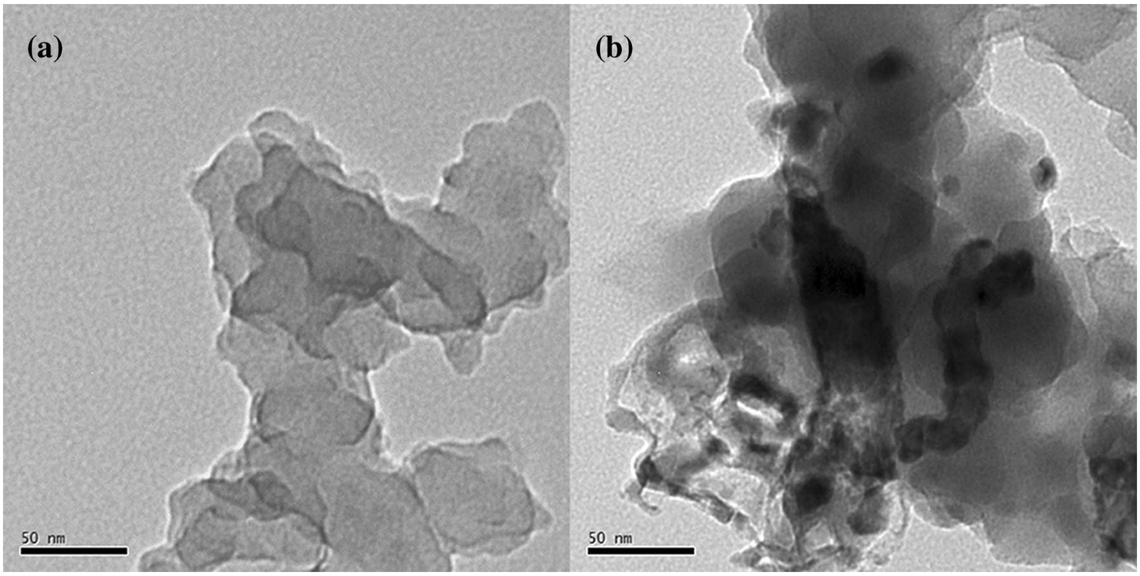


Fig. 7 Transmission electron microscope (TEM) of without catalytic test (**a**) and after 4 catalytic cycles (**b**)

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