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# Synthesis and characterization of mesoporous Pd(II) organometal nanoplatelet catalyst for copper-free Sonogashira reaction in water

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Abstract Periodic mesoporous organopalladium(II)-bridged silica with platelet morphology (Pd(II)-PMO-P) was synthesized the co-condensation of TEOS and bv Pd[PPh<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>Cl<sub>2</sub> using P123 as structure-directing agent. The as-made Pd(II)-PMO-P samples were characterized with XRD, BET, ICP, SEM, TEM, solid NMR, XPS, as well as FT-IR. It was found that these products were composed of platelets (300-400 nm) with short and straight mesoporous channels (100-200 nm). Organopalladium (II) was integrally incorporated into the walls of silica. Compared to the organopalladium(II)-bridged PMO with irregular pore structure, Pd(II)-PMO-P catalyst exhibited high catalytic efficiency in the water-medium Sonogashira reaction because its short pore channels and nano-sized structures could accelerate the diffusion and adsorption of reactant molecules. Furthermore, the heterogeneous catalyst could be reused several times without significant loss of activity, which efficiently decreases the cost as well as the pollution in order to meet the criteria of green chemistry.

Keywords: mesoporous Pd(II) organometal; nanoplatelet; Sonogashira reaction; water-medium

### **1. Introduction**

Since the discovery of M41S, nanostructured mesoporous silica comprises a promising class of catalyst support with singular properties, such as high surface area, pore size uniformity, thermal stability, and synthetic reproducibility [1, 2]. In addition, the material hydrophobicity can be improved by functionalization with alkoxysilane groups bearing ethyl, benzyl, thiol moieties [3, 4]. Previously, we established a new approach to integrally incorporate organometals leading into the silica walls, the to organometal-bridged periodic mesoporous silica[5-7], which further improved the catalytic performance owing to the diminished diffusion limit and also improved the durability of catalyst by inhibiting the leaching of metallic active sites [8-11]. Recently, hierarchically meso-/macroporous nanocatalysts represent an interesting class of solid catalysts since the incorporation of interconnected macropores in mesoporous materials. This kind of mesoporous materials provide an novel platform to fabricate highly active catalysts for the water-medium clean organic synthesis because macropores can favor mass transfer and reduce transport limitations[12]. However, classic mesoporous solid supports, such as SBA-15 possessing the mesostructure of micrometer-long to afford inefficient in-pore diffusion of substrates, resulting in poor catalytic turnover[13, 14]. Obviously, the silica supports with the short pore channels and the regular morphology should be more favorable for the diffusion and adsorption of reactant molecules. Mesoporous organopalladium heterogeneous catalysts with short channels have been reported [11, 15, 16], but most of them were prepared by grafting method or using terminal functionalized silica precursor, leading to the pore blockage for their organic groups terminally bonded to the mesopore wall.

Transition metal mediated cross-coupling reactions have proven to be powerful tools for mild, highly efficient carbon-carbon bond formation [17]. Among these processes, palladium catalyze carbon-carbon coupling reactions, the Sonogashira cross-coupling stands out as a unique method enabling the coupling between (sp) carbon and (sp<sup>2</sup>) carbon atoms[18-22]. The reaction products containing such bonds are important intermediates in organic synthesis, and for the preparation of natural products [23, 24], biologically active molecules [25-28], molecular electronics [28-30], and polymers[31-33]. The original Sonogashira reaction was generally performed in the presence of palladium and copper (I) iodide as a co-catalyst in organic solvents [34]. The presence of copper increases the reactivity of the acetylene by the formation of a copper acetylide. However, Glaser-type oxidative dimerization of the terminalalkynes cannot be avoided in copper-mediated reactions [34], in which side products (diynes) are generally difficult to separate from the desired products, meanwhile copper acetylide is a potentially explosive reagent.

In view of the environmental pollution caused by the use of the hazardous, volatile organic solvents and by-product, the use of an aqueous medium in metal-catalyzed reactions has received considerable attention because water is harmless, non-combustible and readily available. The main advantage of water as a solvent offers simplification of work-up procedures and acceleration of reaction rates[35]. Most studies focused on homogeneous and more expensive palladium complex catalysts for the water-medium Sonogashira reaction due to the relatively low solubility of organic compounds[36-38].

Despite the high activity and selectivity, they were limited in practical application because of the complicated separation procedures from the reaction mixture as well as the difficulties in recycling, which will inevitably lead to high cost and even environmental pollutions from heavy metallic ion[39, 40]. Thus, it is desirable to develop highly efficient heterogeneous palladium catalyst for the copper-free Sonogashira coupling reaction.

Herein, we reported for the first time the uniformly organopalladium(II)-bridged PMO catalysts with platelet morphology (Pd(II)-PMO-P) synthesized by the co-condensation of organopalladium(II)-bridged silane and TEOS using P123 as structure-directing agent. This catalyst showed higher efficiency than the common organopalladium(II)-bridged PMO catalysts (Pd(II)-PMO-T) with irregular shape prepared by traditional method in the water-medium Sonogashira reaction.

# 2. Experimental sections

#### 2.1. Materials

Pluronic P123 ( $EO_{20}PO_{70}EO_{20}$ , M= 5800), 2-(diphenylphos-phino)ethyltriethoxysilane (PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)was obtained from Gelest Inc. and dichlorobis(triphenyl phosphine) palladium(II) (Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>) was purchased from Sigma-Aldrich Company Ltd. Other chemicals used, including tetraethyl orthosilicate (TEOS), ZrOCl<sub>2</sub>·H<sub>2</sub>O, inorganic acids, and organic reagents, were analytically pure and purchased from Sinopharm Chemical Reagent Co., Ltd. The solvents are of analytical quality and dried by standard methods.

2.2. Preparation of mesoporous silica SBA-15-P

Platelet SBA-15 (SBA-15-P) was prepared according to the following procedures. In a typical process, 1.0 g of P123 was dissolved in 45 mL of 2.0 mol/L HCl solution containing 0.32 g of  $ZrOCl_2 H_2O$  at 35 °C. After being completely dissolved, 10 mmol of TEOS was added dropwise slowly. The mixture solution was stirred for 40 min. The mixture was stirred at 35 °C for 24 h and then aged in an autoclave at 100 °C for another 24 h in an oven. Finally, the solid powder filtered and dried was subjected to refluxing in ethanol solution for 24 h at 80 °C to remove P123, leading to the white powder SBA-15-P.

#### 2.3. Catalyst Preparation

In a typical process, Pd(II) organometallicsilane (Pd[PPh<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>Cl<sub>2</sub>) was synthesized in a dry and oxygen-free argon atmosphere using Schlenk techniques[41]. Organopalladium(II)-bridged PMO catalysts with platelet morphology denoted as Pd(II)-PMO-P, adding of was prepared by а certern amount (Pd[PPh<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>Cl<sub>2</sub>) in the platelet SBA-15 synthesis solution. 1.0 g of P123 was dissolved in 45 mL of 2.0 mol/L HCl solution containing 0.32 g of ZrOCl<sub>2</sub>·H<sub>2</sub>O at 35 °C. After being completely dissolved, a certain amount of TEOS was added dropwise slowly. The mixture solution was stirred for 40 min, and then the as-prepared  $Pd[PPh_2(CH_2)_2Si(OC_2H_5)_3]_2Cl_2$  was added. The final reactant molar composition is 0.017 P123: 9.0 HCl: 0.10 Zr: 208 H<sub>2</sub>O: 1.0 Si, where Si referred to the total silica source. The mixture was stirred at 35 °C for 24 h. The mixture was aged, filtrated and treated according to the procedure used in preparing SBA-15-P leading to the primrose powder Pd (II)-PMO-P catalyst. The Pd (II) loading was adjusted by changing the amount of Pd[PPh<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>Cl<sub>2</sub> in the initial mixture, corresponding to Pd (II)-PMO-P-1, Pd (II)-PMO-P-2, and Pd (II)-PMO-P-3.

Pd(II)-PMO-T catalyst was also synthesized by traditional co-condensation method. A certain amount of TEOS was added to the solution contain 1.0 g of P123, 7.5 mL of deionized water and 30 mL of 2.0 mol/L HCl at 35 °C. After being stirred for 40 min, Pd[PPh<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>Cl<sub>2</sub> was added. Then the mixture was stirred for 24 h at the same temperature and aged at 100 °C for another 24 h to get the primrose solid precipitate. The precipitate was filtrated and treated according to the procedure used in preparing Pd (II)-PMO-P.

### 2.4. Catalyst Characterization

Structural characteristics were characterized by X-ray diffraction (XRD, Rigaku D/Max-RB. CuK<sub>a</sub>), scanning electron microscope (SEM, Hitachi S-4800), transmission electron microscopy (TEM, JEOL JEM2100), N<sub>2</sub> adsorption-desorption isotherms (Quantachrome NOVA 4000e) and solid state nuclear magnetic resonance (NMR, Bruker AV-400). Thermo gravimetric analysis and differential thermal analysis (TG/DTA) were conducted on a DT-60. Specific surface areas (S<sub>BET</sub>) and average pore diameter (D<sub>P</sub>) were calculated by using BET and BJH models, respectively. The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ESCA). All the binding energy values were calibrated by using C<sub>1S</sub> = 284.6 eV as a reference. The metal loadings were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, Varian VISTA-MPX).

#### 2.5. Activity Test

The water-medium Sonogashira reaction (Scheme1) of aryl iodide with phenylacetylene was chosen as a probe to evaluate the catalytic performance. It was carried out at 60 °C in a 25 mL Schlenk flask containing a catalyst with 0.0030 mmol of Pd catalyst, 1.0 mmol of iodobenzene, 1.5 mmol of phenylacetylene, 2.0 mmol of triethylamine and 5.0 mL of distilled water. After stirring for 5 h, the products were extracted by ethyl acetate, followed by analysis on a GC-17A gas chromatograph (SHIMADZU) equipped with a JWDB-5, 95% dimethyl 1-(5%)-diphenylpolysiloxane column and a FID detector. The column temperature was programmed from 80 to 250 °C at a speed of 10 °C/min and N<sub>2</sub> was used as carrier gas. The conversions and yields determined on the GC were calibrated by using commercially available samples. The reproducibility was checked by repeating each result at least three times and is found to be within  $\pm$ 5%.

Scheme 1. Sonogashira reaction of phenylacetylene with aryl halide.

#### 2.6. Catalyst recyclability study

In order to determine the durability, the catalyst was allowed to centrifuge after each run of the reactions, following by washed thoroughly with distilled water and ethanol, drying at 80  $^{\circ}$ C overnight under vacuum condition. Then, the catalyst was reused with

fresh charge of water and reactants for subsequent recycling runs under the same reaction conditions.

#### 2.7. Adsorption test

The adsorption for rhodamine B (Rh B) in aqueous solution was taken as a probe to evaluate the adsorption performance of different catalysts. In a typical run of tests, catalyst (100.0 mg) was soaked in water (200 mL) and oscillated at 25 °C for 12 h, followed by adding aqueous solution (50.0 mL) containing 2.50 mg Rh B. The solution was sampled at given time intervals and the concentration of the left Rh B in the solution was determined on an UV-visible spectrophotometer (UV 7504/PC) at the characteristic adsorption wavelength of 523 nm.

#### 3. Results and discussion

3.1. Structural characteristics



Fig. 1. Low-angle XRD patterns of different samples.

The small-angle X-ray diffraction (XRD) patterns of the samples were shown in Fig. 1. All of SBA-15-P and organometal Pd(II) catalyst exhibited three well resolved peaks in the XRD patterns. An intense diffraction around  $2\theta = 0.8 \cdot 0.9^{\circ}$  indicative of (100) plane suggested the 2D *p6mm* hexagonal mesoporous structures [42]. The weak diffraction peaks in higher angle corresponded to (110) and (200) planes, suggesting the ordered mesoporous structure[42], which could be further confirmed by TEM images in Fig. 3. However, the weak diffraction peaks disappeared and the intense diffraction became wider and weaker in Pd (II)-PMO-P-3, suggesting that when Pd(II) loading increased, the mesoporous structure tended to be disordered. It could be due to that the Pd(II) organometallic complexes were mainly embedded in the pore walls and thus reduced the ordering degree of mesoporous structure. The Pd(II)-PMO-P-2 contained well-ordered mesoporous channels similar to the SBA-15-P and Pd(II)-PMO-T.

The ordered mesoporous structures of different samples were further confirmed by nitrogen adsorption-desorption isotherms. As shown in Fig.4, a series of Pd(II)-PMO-P and Pd(II)-PMO-T catalysts exhibited type IV isotherms with H<sub>1</sub>-type hysteresis loops, which represented the mesoporous structures [43-45]. The BET surface area, BJH pore diameter, and pore volume of samples were listed in Table 1.



Fig. 2. FESEM images of Pd (II)-PMO-P-2(a), Pd (II)-PMO-T(b).



Fig. 3. TEM images of Pd (II)-PMO-P-2 (a) and Pd (II)-PMO-T (b).



Fig. 4. N<sub>2</sub> adsorption-desorption isotherms of different samples

#### Table 1

The structure parameters of and catalytic performances of different catalysts in Sonogashira reaction<sup>a</sup>.

Courselo -	Pd Loading	S <sub>BET</sub>	$D_P$	V <sub>P</sub>	Conv.	Yield
Samples	(mmol/g)	(m <sup>2</sup> /g)	(nm)	$(cm^3/g)$	(%)	(%)
SBA-15-P		819	5.3	0.93	0	0
Pd (II)-PMO-P-1	0.24	803	5.2	0.94	92	92
Pd (II)-PMO-P-2	0.43	749	5.2	0.92	96	96
Pd (II)-PMO-P-3	0.58	601	5.1	0.67	89	89
Pd (II)-PMO-P-T	0.42	655	5.3	0.73	83	83

<sup>a</sup>Reaction conditions: a catalyst containing 0.0030 mmol Pd, 1.0 mmol iodobenzene, 1.5 mmol phenylacetylene, 6.0 mmol triethylamine, 5.0 mL  $H_2O$ , 50 °C, 5 h.

The FESEM images in Fig. 2 demonstrated that Pd-PMO-P-2 was present in uniform platelet. The average width and thickness of the platelets were 300-400 nm and 100-200 nm, respectively. Well ordered pores arranged and aligned along the thickness of the thin platelets

are observed on the TEM images (Fig. 3). The platelet morphology and short mesochannels of these materials are quite different from those of Pd-PMO-T, which possessed irregular morphology and long mesochannels in micrometers. It was due to that the Zr(IV) ions increased the average micellar radius of P123 micelles, affected the self-assembly of P123 micelles and further accelerated formation of ordered mesoporus silica[46].



Fig. 5. The XPS spectra of different samples.

The XPS spectra revealed that all the Pd species in the Pd(II)-PMO-P-2 sample were present in +2 oxidation state (Fig. 5), corresponding to the binding energy (BE) of 342.9 and 337.7 eV in the Pd  $3d_{5/2}$  and  $3d_{3/2}$  levels, respectively[47]. In comparison with the BE of the Pd in Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, the BE of the Pd in the Pd(II)-PMO-P-2shifted negatively by 0.3 eV, indicating that the PPh<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-ligand exhibited stronger electron-donation than the PPh<sub>3</sub>-ligand, making Pd atom in the Pd (II)-PMO-P-2 more electron-enriched[47]. It could be also seen from Fig. 5 that all the Pd species in the Pd(II)-PMO-P-2 and Pd(II)-PMO-T

sample had similar chemical environment. The two samples had similar solid NMR spectra as shown in Fig. 6. The <sup>29</sup>Si CP MAS NMR spectrum displayed three resonance up-field peaks corresponding to  $Q^4$  ( $\delta = -110$  ppm),  $Q^3$  ( $\delta = -102$  ppm), and  $Q^2$  ( $\delta = -92$  ppm), and two downfield peaks corresponding to  $T^3$  ( $\delta = -65$  ppm) and  $T^2$  ( $\delta = -57$  ppm). The presence of T<sup>m</sup> peaks indicated the incorporation of the organometal silica moieties as a part of the silica wall structure[48]. Meanwhile, the <sup>13</sup>C CP MAS NMR spectrum showed two peaks at 15 and 58 ppm indicative of two C atoms in the -CH<sub>2</sub>-CH<sub>2</sub>-PPh<sub>2</sub> group. A broad peak around 130 ppm was assigned to the C atoms in the benzene ring[49]. Other peaks marked with asterisks were attributed to rotational sidebands and were confirmed by changing the rotation speed [50]. Besides rotational sidebands marked with asterisks, only one intense peak was observed around 19 ppm in the <sup>31</sup>P CPMAS NMR spectrum of the Pd (II)-PMO-P-2, indicating a unique coordination model between P and Pd(II)[16]. Meanwhile, the TG/DTA curves in Fig. 7 reveal that there is a weak endothermic peak around 100 °C with weight loss of about 14% due to the desorption of water and/or ethanol remaining from solvent extraction processes. The exothermic peak around 300 °C with weight loss of 8 % could be assigned to the oxidation of Pd (II) organometallic complex in the pore channel. The other exothermic peak at 500 °C with the weight loss of 22% was resulted from the oxidation of the phenyl fragments embedded in the pore wall[49]. These results also confirmed the successful incorporation of both the Pd (II) organometallic complexes and the phenyl groups onto the silica support.



Fig. 6. The solid NMR spectra of Pd (II)-PMO-P-2 catalyst.



Fig. 7. TG/DTA curves of Pd (II)-PMO-P-2

#### 3.2. Catalytic Performances

It was summarized that the catalytic activity of different kinds of Pd(II) catalysts performed in the water-medium Sonogashira reactions between iodobenzene and phenylacetylene (Table 1). SBA-15-P was inactive, implying that the Pd(II) active sites were essential for the present reactions. Since no copper salt was used, undesired Glaser-type oxidative homocoupling was avoided, indicating that all these catalysts were almost absolutely selective. From Table 1, it could be seen that the activity of the Pd(II)-PMO-P catalysts with platelet morphology first increased and then decreased with the increase of Pd loading. The Pd(II)-PMO-P-1 catalyst with very low Pd(II) loading (0.24 mmol/g) exhibited poor activity due to the relatively long distance between the neighboring Pd(II) active sites. Taking into account that the Sonogashira reaction needed two kinds of molecules adsorbed on the neighboring Pd(II) active sites, the big space between the neighboring Pd(II) active sites would diminish their synergetic effect. Meanwhile, the Pd(II)-PMO-P-3 with high Pd (II) loading (0.58 mmol/g) also showed poor activity, possibly due to the steric hindrance that retarded the diffusion and even the adsorption of organic molecules on the Pd(II) active sites. So the optimum catalyst was determined as Pd(II)-PMO-P-2 with Pd content of 0.43 mmol/g. Comparing the catalytic performance between Pd(II)-PMO-P-2 and Pd(II)-PMO-P-T with similar Pd loadings, it was obvious that the former showed higher catalytic activity in water-medium Sonogashira reaction, which was further confirmed (Table 2). This could be mainly attributed to the uniform platelet morphology with short mesoporous channels, which facilitate the diffusion and mass transfer of the reactant and product molecules. According to the

adsorption test in Fig. 8, the Pd(II)-PMO-P-2 exhibited not only higher saturated adsorption capacity than the Pd(II)-PMO-T, but also showed faster adsorption rate than Pd(II)-PMO-T, implying that the short pore channels might promoted the diffusion of RhB molecules. Thus, the higher activity of the Pd(II)-PMO-P-2 than that of the Pd(II)-PMO-T could be attributed to both the higher adsorption for reactant molecules and the less diffusion limit.



Fig. 8. Adsorption test of the different catalysts.

In order to verify the higher activity of Pd (II)-PMO-P-2, the Sonogashira reaction of different aryl halide with phenylacetylene was set up (Table 2). As expected, a series of functional groups on the phenyl ring of aryl halides, such as methoxy and nitro, were compatible under this procedure. 4-iodonitrobenzene and 4-bromonitrobenzene containing electron-withdrawing group exhibited higher activity and yield to target products than 4-iodomethoxybenzene, 4-iodomethylbenzene and 4-bromomethoxybenzene containing electron-donating group because the electron-withdrawing groups make the carbon of the

C-I and C-Br bonds more positive which favors the Sonogashira reaction (Table 2, entries 3-8, 11-14).

#### Table 2

Entry	Catalyst	R	Х	Reaction Time	Conv.	Yield (%)	
1	Pd (II)-PMO-P-2	Н	Ι	5	96	96	
2	Pd (II)-PMO-P-T	Н	Ι	5	83	83	
3	Pd (II)-PMO-P-2	OCH <sub>3</sub>	Ι	5	82	82	
4	Pd (II)-PMO-P-T	OCH <sub>3</sub>	Ι	5	67	67	
5	Pd (II)-PMO-P-2	$CH_3$	I	5	84	84	
6	Pd (II)-PMO-P-T	CH <sub>3</sub>	Ι	5	71	71	
7	Pd (II)-PMO-P-2	$NO_2$	Ι	3	97	97	
8	Pd (II)-PMO-P-T	$NO_2$	Ι	3	94	94	
9	Pd (II)-PMO-P-2	Н	Br	8	95	95	
10	Pd (II)-PMO-P-T	Н	Br	8	86	86	
11	Pd (II)-PMO-P-2	CH <sub>3</sub>	Br	11	87	87	
12	Pd (II)-PMO-P-T	$CH_3$	Br	11	74	74	
13	Pd (II)-PMO-P-2	$NO_2$	Br	6	98	98	
14	Pd (II)-PMO-P-T	$NO_2$	Br	6	83	83	

Performances of different catalysts in water-medium Sonogashira reaction<sup>a</sup>

<sup>a</sup>Reaction conditions: a catalyst containing 0.0030 mmol Pd, 1.0 mmol aryl halid, 1.5 mmol phenylacetylene, 2.0 mmol triethylamine, 5.0 mL  $H_2O$ , 60  $^{\circ}C$ .

To make sure whether the heterogeneous or the dissolved homogeneous Pd (II) species was the real catalyst for the coupling reactions, the Sonogashira reaction of 4-nitroiodobenzene and phenylacetylene was chosen as a probe and the following experiments were carried out according to the procedure proposed by Sheldon et al[51].

Firstly, the reaction was allowed to proceed for 2 h until the 4-nitroiodobenzene conversion exceeded 45%. Then, the solid catalyst was filtered out and the mother liquid was allowed to react for another 3 h under the identical reaction conditions. No significant change in the conversion was observed, indicating that the present catalysis was indeed heterogeneous in nature rather than the dissolved Pd (II) species leached from Pd (II)-PMO-P-2.

An important merit of heterogeneous catalysts was their convenient recycling and reuse. As shown in Fig.9, the Pd (II)-PMO-P-2 could be reused in water-medium Sonogashira reaction of 4-iodomethylbenzene with phenylacetylene for at least 7 times without significant decrease in catalytic efficiency, showing good durability of the catalyst. On the one hand, the Pd (II) organometals embedded in silica walls could effectively inhibit the leaching of Pd (II) active sites. According to the ICP analysis, Pd (II) species in the solution was less than 0.5 ppm after being used 7 times, suggesting that the Pd (II)-leaching could be essentially neglected. On the other hand, the Pd (II) organometals embedded in silica walls might also enhance the hydrothermal stability of Pd (II)-PMO-P-2[52]. As shown in Fig. 10, both the low-angle XRD pattern and TEM image demonstrated the preservation of ordered mesoporous structure in the Pd(II)-PMO-P-2 catalyst after being used repetitively for 7 times.



Fig. 9. The recycling tests of Pd(II)-PMO-P-2 catalyst in water-medium Sonogashira reaction.



**Fig. 10.** Low-angle XRD patterns (left) and TEM image (right) of Pd(II)-PMO-P-2 catalyst after being used repetitively for 7 times.

# Conclusions

In summary, a facile approach of surfactant-directed co-condensation for preparing a novel organopalladium(II)-bridged periodic mesoporous organosilica, into which palladium(II) integrally incorporated, was developed. The as-prepared Pd(II)-PMO-P catalyst possessed platelet morphology and ordered mesoporous channels in the range of 300-400 nm, which facilitated the diffusion and mass transfer. The catalyst showed higher activity and stronger durability than traditional Pd(II)-PMO-P-T in water-medium Sonogashira reactions. The Pd(II)-PMO-P could be reused for 7 times without significant deactivation. Other periodic mesoporous organometal silica catalysts including Rh(I), Ru(II), Au(I), Ni(II), etc., could also be designed based on the present method, which may

offer more opportunities for designing powerful immobilized homogeneous catalysts for water-medium clean organic reactions.

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# Highlights

1. A mesoporous organometal Pd(II) catalyst with short channel was synthesized by surfactant-directed co-condensation.

2. The catalyst with active sites inside silica walls was in uniform platelet (300~400 nm).

3. The Pd(II)-PMO-P catalyst exhibited higher efficiency than traditional Pd(II)-PMO-T with irregular shape in water-medium Suzuki reaction.

4. This Pd(II)-PMO-P catalyst could be used repetitively showing the excellent durability.