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Aerosol-Spraying Synthesis of Periodic Mesoporous Organometalsilica Spheres with Chamber Cavities as Active and Reusable Catalysts in Aqueous Organic Reactions

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Organometal-bridged periodic mesoporous catalysts with uniform spheres containing cavities in chambers were synthesized by rapid aerosol-spray assisted co-condensation between organometallic silane and tetraethoxysilane (TEOS) in the presence of cetyltrimethyl ammonium bromide (CTAB) and NaCl double templates. The as-prepared M-PPh₂-PMO(H) catalysts ($M = Pd^{2+}$, Rh⁺ and Ru²⁺) were used in various water-medium organic reactions with the aim of diminishing environmental pollution from organic solvents. These catalysts exhibited high catalytic activities and selectivities owing to the high surface area, the uniform distribution of active sites, the ordered mesoporous channels and especially, the cavities as microreactors which facilitated the diffusion and adsorption of organic reactants. Meanwhile, they also displayed strong durability and could be used repeatedly owing to the organometals incorporated into silica walls and the presence of chamber cavities which could effectively protect the ordered mesoporous structure from damage and also inhibit the leaching of active sites.

1. Introduction

Due to the strong correlation between the physicochemical properties and the shape, size, and structure of materials, the design and preparation of novel nano- and microstructured materials have been intensively pursued not only for fundamental scientific interest but also for their potential applications in various fields.^[1–5] In the past decade, a vast number of inorganic-organic hybrid mesoporous silica materials have been reported and many great successes in practical applications that profited from their high surface area, uniform pore size, and well-defined pore shape have been demonstrated in catalysis, adsorption, separation, sensing, and nanotechnology.^[6–9] However, at first the organo-functionalization was quite limited since the organic groups terminally bonded to the silica pore surface could block pore channels and even destroy the ordered mesoporous

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structure.^[10] Periodic mesoporous organosilica (PMO) with the organic functionalities incorporated into silica walls could effectively diminish pore blockage.^[11] More importantly, the chemical and physical properties of PMO can be tuned by changing the organic functionalities inside the framework, which may offer new opportunities for their applications.^[12] Up to now, various PMO materials containing different functional groups such as ethyl-,^[13] 2-butylene-,^[14] phenyl-,^[15] thiophene-,^[16] and biphenyl^[17] have been synthesized.

Organometals have been widely used in organic synthesis as homogeneous catalysts and recently, they are also employed in water-medium organic reactions with the aim to diminish the environmental pollution from organic solvents.^[18] Despite the high activity and selectivity, there is a problem common in homogeneous cata-

lytic systems: the difficulty of catalyst separation and reuse, which eventually adds cost and even causes environmental pollution from heavy metallic ions.^[19] Immobilized organometallic catalysts can be easily recycled and reused, but they usually display poor activity due to the change in chemical microenvironment of active sites and the enhanced steric hindrance. Previously, we reported organometallic catalysts terminally bonded to mesoporous silica supports, which exhibited high activity, and far exceeded those bonded to traditional supports as a result of the high dispersion of active sites and the low diffusion limit.^[20] Functionalization with organic groups could further promote reaction efficiencies due to the enhanced surface hydrophobicity.^[21] More recently, we developed periodic organometalsilica catalysts with organometals incorporated into silica walls, which showed further improvements in activity and durability owing to the diminished pore blockage and the intensified stability (hydrothermal stability and the stability of the active sites against leaching in catalysis).^[22] However, besides the complicated synthetic process, these catalysts were usually present in irregular shapes with long mesoporous channels, which would inevitably enhance the diffusion limit and also reduce the hydrothermal stability in water-medium organic reactions. Therefore, the development of novel immobilized homogeneous catalysts with high efficiency and strong durability is still the major research topic in both academy or industry.

Herein, we report for the first time a facile approach to synthesize periodic mesoporous organometalsilica with uniform microspheres containing chamber cavities by aerosol-spraying FULL PAPER



Figure 1. Schematic illustration of the preparation of the M-PPh₂-PMO(H) catalyst.

assisted self-assembly in the presence of CTAB (cetyltrimethyl ammonium bromide) and NaCl double templates. During various water-medium organic reactions, these catalysts exhibit higher activity and stronger durability than their corresponding catalysts in solid spheres obtained in the absence of the NaCl that is used to template chamber cavities. The correlation of the catalytic performance to the structural characteristics, especially the promoting effect of the chamber cavities, iss discussed based on the detailed characterizations.

2. Results and Discussion

2.1. Structural Characteristics

Figure 1 illustrates the preparation of organometal-bridged periodic organometalsilica spheres with chamber cavities by one-step aerosol-assisted co-condensation between organometal-bridged silanes (see the structural formula in Figure S1, Supporting Information) and TEOS (tetraethoxysilane) in the presence of CTAB and NaCl double templates (see the preparation details in the Experimental Section).^[23] The as-prepared samples were denoted as *M*-PPh₂-PMO(H), where *M* refers to Pd²⁺, Ru²⁺, Rh⁺ ions, and H to the hollow sphere containing chamber cavities. For comparison, the *M*-PPh₂-PMO(S) spheres without chamber cavities were also synthesized by the same way in the absence of NaCl. Meanwhile, the Pd-PPh₂-MOC-G with Pd(II) organometals terminally bonded to the pore surface was prepared by coordinating metallic ions with the PPh₂-ligands



incorporated into spherical mesoporous silica with chamber cavities obtained by aerosolspraying co-condensation of diphenylphosphino-silane and TEOS using CTAB and NaCl as double templates. In addition, the traditional Pd-PPh₂-PMO in irregular shapes was prepared by P123 surfactant directed cocondensation of Pd(II) organometallic bridged silane and TEOS according to the procedure described elsewhere.^[22a] It should be noted that the Pd-PPh₂-PMO could not be obtained by using CTAB as a template.

The X-ray photoelectron spectroscopy (XPS) spectra (Figure 2a) revealed that all Pd

species in the Pd-PPh₂-PMO(H) catalyst were present in +2 oxidation state, corresponding to the binding energy of 337.5 eV.^[24] In comparison with the Pd(PPh₃)₂Cl₂, the binding energy of the Pd(II) in Pd-PPh₂-PMO(H) shifted negatively by 0.5 eV, possibly due to the stronger electron-donating ability of P atom in the PPh₂-CH₂.CH₂-ligand than that in the PPh₃, taking into account that conjugated π – π system between P and three phenyl groups could dilute the electron density on the P atom.^[25] This could be further confirmed by the XPS analysis of the phosphor element in Pd-PPh₂-PMO(H) sample. As shown in Figure 2b, the binding energy of the phosphor in Pd-PPh₂-PMO(H) shifted positively by 0.6 eV compared to that in the the Pd(PPh₃)₂Cl₂, obviously owing to the stronger electron-donating ability of P atom to Pd in the PPh₂–CH₂–CH₂-ligand than that in the PPh₃-ligand.

Figure 3 shows the solid nuclear magnetic resonance (NMR) spectra of Pd-PPh₂-PMO(H) and Pd(PPh₃)₂Cl₂ catalysts. The ²⁹Si CP MAS NMR spectrum displayed three resonance peaks upfield corresponding to Q⁴ ($\delta = -110$ ppm), Q³ ($\delta = -102$ ppm), and Q² ($\delta = -92$ ppm), and two peaks downfield corresponding to T³ ($\delta = -65$ ppm) and T²($\delta = -57$ ppm), where Qⁿ = Si(OSi)_n-(OH)_{4-n}, n = 2-4 and T^m = RSi(OSi)_m-(OH)_{3-m}, m = 1-3.^[26] The presence of T^m peaks indicates the incorporation of the organometal silica moieties as a part of the silica wall structure. Meanwhile, the ¹³C CP MAS NMR spectrum showed two peaks at 15 and 58 ppm indicative of two C atoms in the –CH₂–CH₂–PPh₂ group. A broad peak around 130 ppm was assigned to the C atoms in the benzene ring.^[27] The ³¹P CP MAS NMR spectrum revealed that, besides the peaks marked with asterisks due to rotational sidebands as confirmed by changing rotational speed, the Pd-PPh₂-PMO(H)



Figure 2. XPS spectra of Pd(PPh₃)₂Cl₂ and Pd-PPh₂-PMO(H) catalysts. a) Pd 3d, b) P 2P.

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Figure 3. Solid NMR spectra of Pd-PPh₂-PMO(H) and Pd(PPh₃)₂Cl₂. The peaks marked with asterisks result from rotational sidebands which was confirmed by changing rotational speed.

exhibited a strong peak around 20 ppm characteristic of the P atom in PPh2-ligand. The similar NMR spectrum of the



Figure 4. TG/DTA curves of Pd-PPh₂-PMO(H).

Pd-PPh₂-PMO(H) to that of PdCl₂(PPh₃)₂ suggests the chemical environment of Pd(II) active sites remained almost unchanged after incorporation into the silica network.^[28] Meanwhile, the TG/DTA curves in Figure 4 reveal that, besides a weak endothermic peak around 80 °C with weight loss of about 4% due to the desorption of water and/or ethanol remaining from solvent extraction processes, the Pd-PPh2-PMO(H) displayed two peaks around 372 °C and 440 °C resulting from the successive breakage of two PPh2-Pd-PPh2 bonds,^[29] corresponding to total weight loss around 14%, in good accordance with the total amount of PPh2-CH2-CH2- groups added in the mother solution for aerosol-spraying. Furthermore, the Pd(II) loading detected by inductively coupled plasma optical emission spectrometer (ICP) was consistent with the total amount of Pd(II) added in the initial solution before aerosol-spraying. All these results demonstrated the successful incorporation of integral Pd-PPh₂ organometals into the silica framework without significant loss of either PPh2-CH₂-CH₂- groups or Pd(II) ions.

Figure 5 reveals that all the Pd-PPh2-PMO(H), Pd-PPh2-PMO(S), Pd-PPh2-MOC-G and traditional Pd-PPh2-PMO samples



Figure 5. N₂ adsorption-desorption isotherms of Pd-PPh₂-PMO(H), Pd-PPh₂-PMO(S), Pd-PPh₂-MOC-G and traditional Pd-PPh₂-PMO catalysts.





Figure 6. Low-angle XRD patterns and N_2 sorption isotherms of Pd-PPh₂-PMO(H), Pd-PPh₂-PMO(S), Pd-PPh₂-MOC-G and traditional Pd-PPh₂-PMO catalysts.

displayed typical type-IV nitrogen adsorption-desorption isotherms with H₁-type hysteresis loops, indicating the presence of mesoporous structure.^[30] The Pd-PPh₂-PMO(H) displayed an additional adsorption at high P/P_0 with a large hysteresis loop, which was due to the emptying of the large internal cavity.^[31] Meanwhile, the low-angle X-ray diffraction (XRD) patterns (Figure 6) showed a well-resolved diffraction peak indicative of the (100) plane of the *p6mm* mesostructure.^[32] The Pd-PPh₂-MOC-G exhibited relatively weak peak intensity in comparison with Pd-PPh2-PMO(H) and Pd-PPh2-PMO(S), suggesting that the oganometals terminally bonded to pore surface reduced the ordering degree of mesoporous structure. Unlike other samples, the traditional Pd-PPh₂-PMO showed principal XRD peak at much lower 2θ , implying the large diameter of mesoporous channels, which could be attributed to the use of P123 instead of CTAB as the template. According to the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images in Figure 7, both the Pd-PPh2-PMO(H) and the Pd-PPh2-PMO(S) comprised of uniform spheres with average size



Figure 7. a) SEM and b,c) TEM images of Pd-PPh₂-PMO(H) and d) TEM image of Pd-PPh₂-PMO(S).



around 400 nm. The Pd-PPh2-PMO(H) displayed cubic cavities with diameter around 60 nm in the sphere chamber while the Pd-PPh₂-PMO(S) prepared in the absence of NaCl displayed no cavities inside the sphere chamber. These results clearly demonstrate that NaCl crystals templated the cubic cavities in chamber, which could also account for the presence of chamber cavities observed in PPh2-MOC and Pd-PPh2-MOC-G (see Figure S2). The high-magnification TEM image in Figure 7 clearly displayed ordered mesoporous channels in silica walls. The SEM and TEM images (Figure S3 and S4) showed that both Ru-PPh₂-PMO(H) and Rh-PPh2-PMO(S) samples also comprised uniform spheres with ordered mesoporous structure in the silica wall and cavities in the chamber. The ordered mesoporous structure was further confirmed by low-angle XRD patterns (Figure S5), nitrogen adsorption-desorption isotherms (Figure S6), and pore size distribution curves (Figure S7). TEM images revealed that the traditional Pd-PPh2-PMO also contained ordered mesoporous channels (Figure S8). However, unlike the other three samples, it was present in irregular shapes.

The metallic species incorporated into silica walls of the M-PPh₂-PMO(H) spheres should be chemically accessible to the reactant molecules since they act as active sites in catalysis. To determine the chemical accessibility of the Rh-PPh₂-PMO(H), it was allowed to react with KMnO₄ aqueous solution. Only the Rh(I) organometals chemically accessible could be oxidized by KMnO₄ while those Rh(I) species embedded in silica walls could not be oxidized.^[33] After complete reaction, the unreacted KMnO₄ was titrated by Na₂C₂O₄, from which the amount of Rh(I) species were also determined by ICP analysis. The molar ratio between Rh(I) species determined by KMnO₄ oxidation and ICP was 94%, suggesting that most of Rh(I) active sites in the Rh-PPh₂-PMO(H) were chemically accessible for catalytic reactions.

By applying the multiple-point Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) models on the adsorption branches of nitrogen adsorption-desorption isotherms, respectively, the specific surface area (S_{BET}), the average pore diameter (D_p) and pore volume (V_p) were calculated. As shown in Table 1, the Pd-PPh2-PMO(H) and the Pd-PPh2-PMO(S) exhibited much smaller $D_{\rm P}$ than the traditional Pd-PPh2-PMO due to the different surfactant templates (CTAB vs P123). However, they still displayed higher S_{BFT} and V_{P} since they were present in small spheres containing more mesopores. Although having the same D_P, the Pd-PPh₂-PMO(H) exhibited higher S_{BET} and V_{P} than the Pd-PPh₂-PMO(S), obviously owing to the presence of chamber cavities. Meanwhile, the Pd-PPh₂-MOC-G displayed much lower S_{BET} , V_{P} and D_{P} than either the Pd-PPh2-PMO(H)or the Pd-PPh2-PMO(S) since the organometals terminally bonded to the pore surface may partially block the pore channels.[34]

2.2. Catalytic Performances

Water-medium Barbier reaction, Sonogashira reaction, terminal alkynes acylation, Suzuki reaction, isomerization, and Miyaura-Michael reaction (**Scheme 1–6**) were used as probes to evaluate the catalytic performances of the as-prepared catalysts (see



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Table 1. Structural parameters and catalytic performances of different Pd(II)-based catalysts in water-medium Barbier reaction betweenp-chlorobenzaldehyde and allyl bromide.^{a)}

Catalysts	Pd Loading [wt%]	S _{BET} [m ² g ⁻¹]	D _P [nm]	V _P [m ³ g ⁻¹]	Conversion [%]	Selectivity [%]	Yield [%]
Pd-PPh ₂ -PMO(H)-1	1.2	1674	3.2	0.90	87	88	76
Pd-PPh ₂ -PMO(H)	1.5	1585	3.1	0.84	95	95	90
Pd-PPh ₂ -PMO(H)-2	2.2	1556	3.0	0.87	81	92	76
Pd-PPh ₂ -PMO(S)	1.5	1504	3.1	0.71	88	91	80
Pd-PPh ₂ -MOC-G	3.7	1108	2.7	0.64	80	91	73
Pd-PPh ₂ -PMO	1.6	780	7.8	0.72	82	90	73
$Pd(PPh_3)_2Cl_2$	/	/	/	/	98	92	90

^{a)}Reaction equation and conditions are given in Scheme 1 and the Experimental Section.



Scheme 1. Water-medium Barbier reaction between substituted benzaldehyde and allyl halide.



Scheme 2. Water-medium Sonogashira reaction between phenylacetylene and different substituted iodobenzenes.



Scheme 3. Water-medium terminal alkynes acylation reaction between benzoyl chloride and phenylacetylene.



Scheme 4. Water-medium Suzuki cross-coupling reaction of arylboronic acid and aryl halide.



Scheme 5. Water-medium isomerization reaction of 1-phenyl-3-buten-1-ol.



Scheme 6. Water-medium Miyaura-Michael reaction of phenylboronic acid and butyl acrylate.

experimental details in the Experimental Section). As shown in Table 1, all the Pd(II) based organometallic catalysts exhibited the equivalent selectivities in water-medium Barbier reaction

between *p*-chlorobenzaldehvde and allvl bromide, implying the similar nature and chemical micro-environment of the active sites. Obviously, the Pd-PPh2-PMO(H) was most active among all the immobilized Pd(II) organometallic catalysts. The timeconversion curves (Figure S9) also confirmed that Pd-PPh₂-PMO(H) exhibited higher activity than Pd-PPh₂-PMO(S). The higher activity of the Pd-PPh₂-PMO(H) than that of the Pd-PPh₂-PMO(S) could be mainly attributed to promoting effect of the chamber cavities since these two catalysts contained the same ordered mesoporous structure with identical pore diameters. Besides the slight increase in S_{BET} , the presence of chamber cavities could act as micro-reactor which shortened the pore channels and thus, facilitated the diffusion of reactant and product molecules.^[35] It could be further confirmed by adsorption test of rhodamine B (see the detailed procedure in the Experimental Section). As shown in Figure 8a, the Pd-PPh₂-PMO(H) displayed much higher saturated adsorption capacity (64%) than the Pd-PPh₂-PMO(S) (39%), in good accordance with the surface area (S_{BET}) and pore volume (V_P) values (see Table 1). Straight lines were obtained by plotting 1/C vs t (Figure 8b), where C refers to the concentration of rhodamine B in the solution after adsorption for t hour, indicating the second order of the adsorption reaction. Thus, the adsorption rate of reactant molecules possibly played an important role in determining the reaction activity. According to the tangent slopes, the adsorption constants (k) of Pd-PPh₂-PMO(H) and Pd-PPh₂-PMO(S) catalysts were determined as 0.042 and 0.021, respectively, showing that the Pd-PPh₂-PMO(H) adsorbed organic molecules more rapidly than the Pd-PPh2-PMO(S). These results also demonstrated that presence of chamber cavities in the Pd-PPh₂-PMO(H) spheres promoted the adsorption for organic reactant molecules, leading to the enhanced activity.^[36]

It was also found that the Pd-PPh₂-PMO(H) was more active than the Pd-PPh₂-MOC-G. Taking into account that both two catalysts contained similar chamber cavities, the higher activity of the Pd-PPh₂-PMO(H) could be mainly attributed to its big pore size since the organometals were incorporated into silica walls. However, the organometals were terminally bonded to the pore surface in the Pd-PPh₂-MOC-G, which partially blocked the pore channels, leading to the decrease in pore diameter (see the D_P values). In addition, both the Pd-PPh₂-PMO(H) and the Pd-PPh₂-PMO(S) exhibited higher activity than the traditional







Figure 8. Adsorption profiles of Pd-PPh₂-PMO(S) and Pd-PPh₂-PMO(H) catalysts with the adsorption time (h). The adsorption capacity refers to the change of $(C_0-C)/C_0$ with the adsorption time (h), where C_0 refers to the initial concentration of rhodamine B in the solution before adsorption and C to the concentration of rhodamine B after adsorption.

Pd-PPh₂-PMO, though the Pd-PPh₂-PMO contained mesoporous channels with bigger diameter. This could be mainly attributed to the uniform spheres of the Pd-PPh₂-PMO(H) and the Pd-PPh₂-PMO(S), taking into account that the Pd-PPh₂-PMO was present in irregular shapes with longer average pore channels, which maybe disfavor the diffusion of reactant molecules.^[37] More interesting, the Pd-PPh₂-PMO(H) exhibited comparable activity and selectivity with homogeneous PdCl₂(PPh₃)₂, which could also be observed in water-medium Barbier reactions with other reactants (**Table 2**) and Sonogashira reactions of phenylacetylene with different substituted iodobenzenes (**Table 3**).

Table 4 further demonstrated that all the *M*-PPh₂-PMO(H) $(M = Pd^{2+}, Ru^{2+}, Rh^+)$ catalysts with the chamber cavities were more active than their corresponding *M*-PPh₂-PMO(S) without chamber cavities in water-medium terminal alkynes acylation reaction, Suzuki reaction, isomerization reaction and

Table 2. Catalytic performances of Pd-PPh₂-PMO(H) and Pd(PPh_3)_2Cl_2 in water-medium Barbier reactions with different reactants.^{a)}

	+	Pd	(II)-Catalyst	OH	
R		Λ		R	
Catalyst	R	Х	Conversion [%]	Selectivity [%]	Yield [%]
Pd-PPh ₂ -PMO(H)	Cl	Cl	98	78	76
$Pd(PPh_3)_2Cl_2$			97	75	73
Pd-PPh ₂ -PMO(H)	Cl	I	99	99	98
$Pd(PPh_3)_2Cl_2$			99	95	95
Pd-PPh ₂ -PMO(H)	CH_3	Br	94	88	83
$Pd(PPh_3)_2Cl_2$			91	90	82
Pd-PPh ₂ -PMO(H)	н	Br	91	93	85
$Pd(PPh_3)_2Cl_2$			92	94	86
Pd-PPh ₂ -PMO(H)	CH_3	Cl	87	75	65
Pd(PPh ₃) ₂ Cl ₂			89	76	68

^{a)}Reaction conditions are given in the Experimental Section.

Table 3. Catalytic performances of heterogenized and homogeneous Pd(II) organometallic catalysts in water-medium Sonogashira reaction.^{a)}

R-{	- () -	d(II)-Catalyst	<hr/>	R
Catalysts	R	Conversion [%]	Selectivity [%]	Yield [%]
Pd(PPh ₃) ₂ Cl ₂	н	97	97	94
Pd-PPh ₂ -PMO(H)		98	98	96
$Pd(PPh_3)_2Cl_2$	CH_3	98	97	95
Pd-PPh ₂ -PMO(H)		98	97	95
$Pd(PPh_3)_2Cl_2$	NO ₂	97	100	97
Pd-PPh ₂ -PMO(H)		99	98	97

^{a)}Reaction conditions are given in the Experimental Section.

Miyaura-Michael reaction, respectively. These M-PPh₂-PMO(H) catalysts exhibited comparable activities and selectivities with the corresponding homogeneous catalysts, obviously owing to the high surface area, the uniform distribution of active sites, the ordered mesoporous channels and especially, the cavities as microreactors which facilitated the diffusion and adsorption of organic reactants. To make sure the M-PPh2-PMO(H) was the real heterogeneous catalyst, the Barbier reaction between p-chlorobenzaldehyde and allyl bromide and allyl bromide was chosen as a probe and the following experiments were carried out according to the procedure proposed by Sheldon et al.^[38] Firstly, the reaction was allowed to proceed for 6 h until the benzaldehyde conversion exceeded 50%. Then, the reaction mixture was filtered to remove the solid catalyst and the mother liquor was allowed to react for another 12 h under identical conditions. No significant change in either the conversion of *p*-chlorobenzaldehyde or the yield of target product p-chlorobenzene-3-buten-1-ol was observed. These results clearly demonstrated that the present catalysis indeed was



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Table 4. Catalytic performances of different catalysts in various water-medium organic reactions.^{a)}



^{a)}Reaction conditions are given in the experimetanl section.

heterogeneous in nature rather than the dissolved Pd(II) species leached from *M*-PPh₂-PMO(H).

An important merit of heterogeneous catalysts is that they should be conveniently recycled and reused.^[39] As shown in Figure 9, the Pd-PPh₂-PMO(H) catalyst could be reused at least 10 times without significant decrease in catalytic activity, while the Pd-PPh2-MOC-G or the traditional Pd-PPh2-PMO could be reused only for 5 times. According to the ICP analysis, the Pd-PPh2-MOC-G displayed 17% Pd(II) leaching while both the Pd-PPh₂-PMO(H) and the traditional Pd-PPh₂-PMO displayed no significant Pd(II) leaching after being used repeatedly for 5 times. The high stability of the Pd-PPh₂-PMO(H) and the traditional Pd-PPh₂-PMO catalysts against leaching of Pd(II) active sites could be mainly attributed to the organometals incorporated into the silica walls. The TEM images (Figure 10) demonstrate that the Pd-PPh₂-PMO(H) remained ordered mesoporous structure and chamber cavities while the Pd-PPh2-MOC-G showed partial damage of mesoporous structure, suggesting that the organometals incorporated into the silica walls could enhance the hydrothermal stability of the mesoporous structure.^[40] Although the traditional Pd-PPh₂-PMO also contained the organometals incorporated into the silica walls, it displayed much more remarkable damage of the ordered mesoporous structure, implying that the presence of chamber cavities could effectively protect the ordered mesoporous structure from



Figure 9. The recycling tests of different catalysts in water-medium Barbier reaction between *p*-chlorobenzaldehyde and allyl bromide. Reaction conditions are given in the Experimental Section.

damage since they could shorten the pore channels which accelerated both the adsorption of reactant molecules and the desorption of product molecules. From these results, we conclude that the decrease in the activity of the traditional Pd-PPh₂-PMO



Figure 10. TEM images of a) Pd-PPh₂-PMO(H), b) Pd-PPh₂-MOC-G, and c) Pd-PPh₂-PMO catalysts after being used repeatedly for 5 times.





after being reused for 5 times can be mainly attributed to severe damage of ordered mesoporous structure. The Pd-PPh₂-MOC-G catalyst lost its activity after being reused for 5 times due to both the partial damage of ordered mesoporous structure and the leaching of Pd(II) active sites. The Pd-PPh₂-PMO(H) exhibited excellent durability owing to its strong stability against both the damage of ordered mesoporous structure and the leaching of Pd(II) active sites.

3. Conclusions

In summary, we have developed an aerosol-spraying approach for rapidly synthesizing periodic organosilica catalysts with organometals incorporated into silica walls in uniform spheres containing cavities inside the chamber. These catalysts exhibited comparable activity with the corresponding homogeneous catalysts and strong durability in various water-medium organic reactions. The presence of chamber cavities played a key role in promoting activity and enhancing stability against both damage of the ordered mesoporous structure and the leaching of metallic active sites. The present strategy is general for designing powerful heterogenized organometallic catalysts in clean organic synthesis, which might offer more opportunities for their practical applications.

4. Experimental Section

Catalyst Preparation: In a typical run of synthesis, CTAB (1.60 g, 5.2 mmol), NaCl (0.39 g, 6.7 mmol), ethanol (58 mL), H₂O (10 mL), HCl aqueous solution (2.0 mol L⁻¹, 0.22 mL) and certain amount of TEOS were mixed and allowed pre-hydrolysis for 1 h at room-temperature. Then, 2.0 mL of THF solution containing required amount of organometal-bridged silane was added into the mixture. After being stirred for 1 h, the solution was allowed to pass through atomizer and tube furnace of aerosol-spraying reactor by N₂ carrier gas. The obtained solid product refluxed in 500 mL of ethanol solution containing HCl (0.50 mol L⁻¹) at 80 °C for 24 h to remove surfactant, NaCl and other organic substances, leading to *M*-PPh₂-PMO(H), where $M = Pd^{2+}$, Rh⁺, and Ru²⁺.

Catalyst Characterization: Structural characteristics are characterized by NMR spectra (Bruker AV-400), XRD patterns (Rigaku D/Max-RB. CuK α), TEM images (JEOL JEM2100), and N₂ adsorption–desorption isotherms (Quantachrome NOVA 4000e). Specific surface areas (S_{BET}) and average pore diameter (D_P) are 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 are calibrated by using C1S = 284.6 eV as a reference. The metal loadings are determined by ICP analysis (Varian VISTA-MPX). The spectrophotometric determination of dyes was done on UV–vis spectrophotometer (Shimadzu UV-2100S).

Activity Test: Generally, each run of organic reactions was carried out in a 10 mL round-bottomed flask. The reaction equations were listed in Scheme 1–6. The reproducibility was confirmed after repeating experiments for at least three times and was found to be within acceptable limits (\pm 5%). The detail reaction conditions and the product analysis were as follows:

Barbier reaction (Scheme 1): A catalyst containing Pd(II) (0.050 mmol), p-chlorobenzaldehyde (0.025 mL), allyl bromide (0.15 mL), H_2 O (5.0 mL), SnCl₂ (0.45 g, 2.4 mmol), reaction temperature = 50 °C, reaction time = 12 h. The products were extracted with toluene for GC analysis (Agilent 1790) equipped with a JWDB-5, 95% dimethyl 1-(5%)-diphenylpolysiloxane column and a FID detector under column temperature of 100 °C in N₂ flow as carrier gas. The reaction conversion

was calculated by using p-chlorobenzaldehyde since allyl bromide was excess.

Sonogashira reaction (Scheme 2): A catalyst containing Pd(II) (0.0020 mmol), iodobenzene (0.14 mL), phenylacetylene (0.11 mL), DBU (0.29 mL), water (2.0 mL), reaction temperature = 70 °C, reaction time = 2 h. The products were extracted with toluene for GC analysis (SHIMADZU) equipped with a JWDB-5, 95% dimethyl 1-(5%)-diphenylpolysiloxane column and a FID detector in N₂ flow as carrier gas. The column temperature was programmed from 100 to 250 °C. The reaction conversion was calculated based on phenylacetylene since iodobenzene was excess.

Acylation reaction (Scheme 3): A catalyst containing Pd(II) (0.050 mmol), phenylacetylene (0.28 mL), benzoyl chloride (0.58 mL), Cul (0.025 g, 0.13 mmol), K₂ CO₃ (1.0 g, 7.2 mmol), sodium lauryl sulfate (0.050 g, 0.17 mmol), and water (2.5 mL), reaction temperature = 65 °C, reaction time = 4 h. The products were extracted with toluene for GC analysis under the former conditions. The reaction conversion was calculated by using phenylacetylene since benzoyl chloride was excess.

Suzuki reaction (Scheme 4): A catalyst containing Pd(II) (0.013 mmol), phenylboronic acid (0.024 g, 0.20mmol),1-iodo-4-nitrobenzene (0.075 g, 0.30mmol), K₂ CO₃ (0.10 g), CuI (0.0010 g, 0.72mmol), H₂ O (3.0 mL), reaction temperature = 70 °C, reaction time = 12 h. The products were extracted with toluene for GC analysis under the former conditions. The reaction conversion was calculated by using 1-iodo-4-nitrobenzene since phenylboronic acid was excess.

Isomerization reaction (Scheme 5): A catalyst containing Ru(II) (0.014 mmol), 1-phenyl-3- buten-1-ol (0.025 mL), H₂ O (5.0 mL), reaction temperature = 100 °C, reaction time = 8 h. The products were extracted with ether and dried by MgSO₄, followed by removing solid and solvent via filtration and evaporation. The products were identified by ¹ H NMR spectroscopy. Quantitative analysis was performed on a HPLC (Shimadzu SPD-10AVP) equipped with a UV-vis detector and a KR100-5C18 column.

Miyaura-Michael reaction (Scheme 6): A catalyst containing Rh(I) (0.0078 mmol), butyl acrylate (0.075 mL), phenylboronic acid (0.013 g, 0.11mmol), H₂ O (6.0 mL), reaction temperature = 100 °C, reaction time = 5 h. The products were extracted with toluene for GC analysis (SHIMADZU) equipped with a JWDB-5, 95% dimethyl 1-(5%)-diphenylpolysiloxane column and a FID detector in N₂ flow as carrier gas. The column temperature was programmed from 80 to 250 °C. The reaction conversion was calculated by using butyl acrylate since butyl phenylboronic acid was excess.

In order to determine the durability, the catalyst was allowed to centrifuge after each run of the reactions, which was washed thoroughly with distilled water and toluene, followed by drying at 353 K for 8 h under vacuum condition. Then, the catalyst was re-used with fresh charge of water and reactants for subsequent recycle runs under same reaction conditions.

Adsorption Test: To test the adsorption behaviors, 200 mg catalyst was soaked in 200 mL water and oscillated at 25 °C for 12 h, followed by adding 50.0 mL aqueous solution containing 50.0 mg L⁻¹ rhodamine B. The solution was sampled at given time intervals and the concentration of the left rhodamine B in the solution was determined on a UV-visible spectrophotometer (UV 7504/PC) at the characteristic adsorption wavelength of 523 nm. The adsorption capacity was determined after reaching saturation adsorption. According to the change of rhodamine B concentration (*C*) with the time (*t*), the adsorption kinetics was studied based on the adsorption equation d*C*/dt = kCⁿ, where kn and refer to the adsorption rate constant and adsorption order, respectively. The adsorption capacity was determined after reaching saturation adsorption.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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