

Periodic Mesoporous Organometallic Silicas with Unary or Binary Organometals inside the Channel Walls as Active and Reusable Catalysts in Aqueous Organic Reactions

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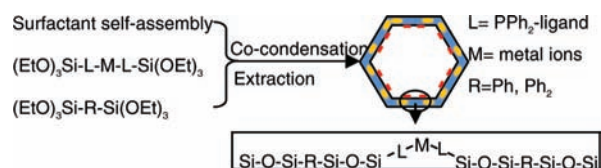
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Organometallic catalysts are widely used in organic synthesis owing to high activity and selectivity.¹ Recently, they have also been explored in water-medium reactions, an important aspect of green chemistry.² However, their applications in aqueous medium are still limited by their reduced catalytic efficiency and difficulties in recycling and subsequent reuse, which eventually increase costs and cause heavy metal pollution.³

Immobilization of organometals onto nanomaterials represents an attractive strategy for catalyst recycling.⁴ Nevertheless, the heterogenized catalyst usually exhibits lower activity and selectivity than the homogeneous catalyst due to poor dispersion of active sites, the enhanced steric hindrance, and the change of chemical microenvironment of the active sites.⁵ Previously, we reported the immobilized organometallic catalysts on the mesoporous silica functionalized with organic groups, which exhibited enhanced activity in water-medium organic reactions owing to the high dispersion of active sites and the enhanced surface hydrophobicity. However, the presence of organometals and organic groups terminally bonded to the pore surface blocks the pore channels and induces significant metal leaching.⁶ Herein, we wish to disclose new periodic mesoporous organometallic silicas containing bridge-bonded organometals and organic groups directly integrated into the silica framework, denoted as M-PPh₂-PMO(R), where M refers to Pd²⁺, Au⁺, Ru²⁺, and Rh⁺ ions, PPh₂ to PPh₂CH₂CH₂-ligands, and R to phenyl (Ph) or biphenyl (Ph₂) groups. As demonstrated, these catalysts display comparable activities with the corresponding homogeneous catalysts in water-medium organic reactions and can be used repetitively without a significant loss of activity.

A general approach for the preparation of M-PPh₂-PMO(R) is illustrated in Scheme 1. First, organometal-bridged silanes are synthesized by coordinating metallic ions with PPh₂CH₂CH₂Si(OEt)₃ (see the structural formula in Figure S1). Their compositions and purities are determined by both ICP analysis and NMR spectra (Figure S2). The organometal-bridged silanes are allowed to coassemble with R-bridged silane and P123 surfactant. Removal of surfactant micelles via extraction in ethanol leads to the M-PPh₂-PMO(R) samples. In parallel, the grafted M-PPh₂-PMO(R)-G are synthesized for comparison studies by coordinating metallic ions with the PPh₂-ligands originally anchored on the PMO(Ph) via surfactant directed co-condensation between bis(triethoxysilyl)benzene and 2-(diphenylphosphino)ethyltriethoxysilane. Meanwhile, M-PPh₂-SBA-15 and M-PPh₂-SBA-15(Ph) are prepared by co-condensation between organometal-bridged silane and tetraethylorthosilicate or phenyltrimethoxysilane in the presence of P123 (see Supporting Information for details). Moreover, commercially available homogeneous organometal catalysts are directly used for comparison studies.

Scheme 1. Preparation of M-PPh₂-PMO(R) by Surfactant-Directed Co-Condensation



The FTIR and Raman spectra (Figures S3 and S4) of Pd-PPh₂-PMO(Ph) samples displayed no significant absorbance characteristic of a P123 molecule, indicating the almost complete removal of surfactant template after extraction in ethanol.⁷ Compared with PMO(Ph), Pd-PPh₂-PMO(Ph) shows three additional peaks around 2890, 2980, and 1527 cm⁻¹ due to vibrations from C–H and C–P in the CH₂–CH₂ and PPh₂ groups.⁸ The Raman peaks around 777, 1324, 1598, 1028, and 997 cm⁻¹ also confirm the presence of phenyl, Pd–P, and P–C groups.⁹ These results demonstrate the successful incorporation of both Pd-PPh₂CH₂CH₂ and the phenyl into silica walls, which is further confirmed by solid NMR spectra (Figure S5). The ²⁹Si CP-MAS NMR displays only three low-field peaks corresponding to T³ (δ = –79 ppm), T² (δ = –73 ppm), and T¹ (δ = –63 ppm), indicating that all Si species are covalently bound to carbon.¹⁰ The ¹³C CP-MAS NMR displays three peaks at 13 and 58 ppm corresponding to C1, C2', and C1' atoms and the other peak at 33 ppm to C2, which is overlapped by the rotational band peak. An intense peak at 133 ppm is assigned to the C atoms in the benzene ring. The ³¹P CP-MAS NMR displays only one signal at 20.6 ppm, suggesting the unique Pd-PPh₂ coordination bond.¹¹

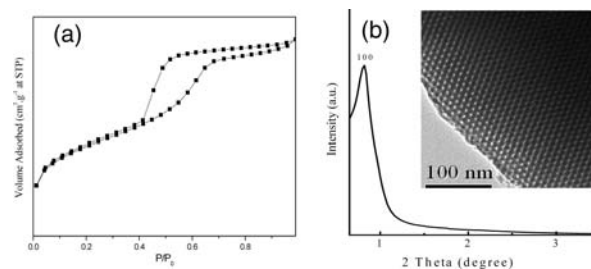


Figure 1. N₂ sorption isotherm (a) and low-angle XRD pattern (b) of the Pd-PPh₂-PMO(Ph) sample. The inset is the TEM image.

As shown in Figure 1, Pd-PPh₂-PMO(Ph) displays a type IV nitrogen adsorption–desorption isotherm with the H₂ hysteresis loop while the low-angle XRD pattern exhibits a well resolved peak at 2θ = 0.8°–1.0°, a (100) diffraction, indicating the ordered two-dimensional P6mm hexagonal mesoporous channels,¹² which is further verified by the TEM image (see Figure S6 for other samples). From Table 1, one can conclude that the

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Pd(II) complexes in Pd-PPh₂-PMO(Ph) are embedded in the pore walls rather than terminally bonded to the pore surface, which effectively diminishes pore channel blockage, leading to higher S_{BET} and D_p than those of the grafted Pd-PPh₂-PMO(Ph)-G with an equivalent Pd loading. Although Pd-PPh₂-PMO(Ph₂) displays a similar mesoporous structure to that of Pd-PPh₂-PMO(Ph) (see Figure S7), the wide-angle XRD patterns (Figure S8) demonstrate the crystal-like pore walls rather than the amorphous pore walls, possibly as a result of the π - π stacking of biphenyl groups.¹³

As revealed in Table 1, Pd-PPh₂-PMO(Ph) exhibits much higher activity and selectivity than corresponding Pd-PPh₂-PMO(Ph)-G, Pd-PPh₂-SBA-15(Ph), and Pd-PPh₂-SBA-15 in water-medium Barbier reactions with the same amount of Pd(II) used (see Scheme S1), obviously owing to the higher S_{BET} , the larger D_p , and the enhanced surface hydrophobicity resulting from the Ph-modification, which facilitates the diffusion and adsorption of organic reactants,¹⁴ especially in a water medium. Despite the lower S_{BET} and D_p , Pd-PPh₂-PMO(Ph₂) exhibits similar activity to that of Pd-PPh₂-PMO(Ph) as a result of the Ph₂-modified stronger surface hydrophobicity. Remarkably, Pd-PPh₂-PMO(Ph) displays comparable efficiencies in Barbier and Sonogashira reactions with the homogeneous Pd(PPh₃)₂Cl₂ (Tables S1 and S2). Similar results are also observed for Au-PPh₂-PMO(Ph), Rh-PPh₂-PMO(Ph), and Ru-PPh₂-PMO(Ph) catalysts (see Table 2). According to a standard procedure developed by Sheldon et al.,¹⁵ the Pd-PPh₂-PMO(Ph) catalyzed Barbier reaction is allowed to proceed for 6 h with conversion exceeding 45%. After removing the solid catalyst, the mother solution is allowed to react for another 12 h under identical conditions. No significant change in either the conversion or the product yield has been observed, indicating that the present catalysis indeed is heterogeneous in nature rather than the dissolved Pd(II) species leached from solid Pd-PPh₂-PMO(Ph).

Table 1. Structural Parameters and Catalytic Performances of Organometallic Catalysts in Water-Medium Barbier Reaction

Catalyst	Pd loading (wt%)	S_{BET} (m ² /g)	D_p (nm)	Conv. (%)	Select. (%)
Pd-PPh ₂ -SBA-15	0.85	389	3.9	56	71
Pd-PPh ₂ -SBA-15(Ph)	0.54	145	1.7	61	88
Pd-PPh ₂ -PMO(Ph)-G	1.7	438	3.6	78	91
Pd-PPh ₂ -PMO(Ph)	1.7	654	5.7	93	96
Pd-PPh ₂ -PMO(Ph ₂)	3.9	444	3.3	92	95
Pd(PPh ₃) ₂ Cl ₂	/	/	/	96	94

Table 2. Structural Parameters and Catalytic Performances of Organometallic Catalysts in Various Water-Medium Organic Reactions

Catalyst	Loading (wt%)	S_{BET} (m ² /g)	D_p (nm)	Reaction	Yield (%)
Au(PPh ₃)Cl	/	/	/	Hydration	26
Au-PPh ₂ -PMO(Ph)	0.22	892	3.1	Scheme S2	91
Grafted Au-PPh ₂ -PMO(Ph)	0.26	561	2.8		24
Rh(PPh ₃)Cl	/	/	/	Heck	86
Rh-PPh ₂ -PMO(Ph)	0.42	606	3.7	Scheme S3	84
Grafted Rh-PPh ₂ -PMO(Ph)	0.47	513	3.2		71
Ru(PPh ₃) ₂ Cl ₂	/	/	/	Isomerization	75
Ru-PPh ₂ -PMO(Ph)	0.40	589	3.8	Scheme S4	77
Grafted Ru-PPh ₂ -PMO(Ph)	0.43	479	2.9		58

As shown in Figure 2, Pd-PPh₂-PMO(Ph) exhibits stronger durability than the grafted Pd-PPh₂-PMO(Ph)-G. This could be attributed to the incorporation of Pd(II) organometals into the silica walls, which effectively inhibits the leaching of the Pd(II) active phase and also enhances the hydrothermal stability¹⁶ (see Table S3). Pd-PPh₂-PMO(Ph₂) is even more durable than Pd-PPh₂-PMO(Ph) since the crystal-like pore walls exhibit strong hydrothermal stability than the amorphous pore walls,¹³ leading to the preservation of ordered mesoporous structure even after 10 recycled tests (see Figure S9).

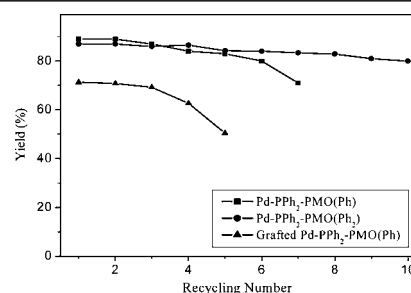


Figure 2. Recycling tests of the grafted Pd-PPh₂-PMO(Ph), Pd-PPh₂-PMO(Ph), and the Pd-PPh₂-PMO(Ph₂) catalysts in Barbier reactions.

The assembly strategy has been successfully applied in the synthesis of a novel bifunctional catalyst with Pd(II) and Ru(II) organometals homogeneously inside ordered mesopore walls by co-condensation of Pd(II) and Ru(II) organometal-bridged silanes with bis(triethoxysilyl)-benzene and P123 (see Figure S10). Impressively, such Pd@Ru-PPh₂-PMO(Ph) exhibits comparable efficiency with Pd(PPh₃)₂Cl₂/Ru(PPh₃)₃Cl₂ in a water-medium “one-pot” Barbier-isomerization cascade reaction and could be reused for at least 7 times (Figure S11).

In summary, we have developed a novel approach for the preparation of ordered mesoporous organometallic catalysts with organometals embedded in silica walls. Notably, they exhibit high catalytic efficiencies and strong durability in water-medium organic reactions. Moreover, bifunctional catalysts containing two kinds of organometals can also be synthesized and explored in “one-pot” cascade reactions. The strategy described in the study serves as a general approach for immobilization of homogeneous catalysts with broad and practical applications.

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Supporting Information Available: Experimental procedures and characterization of the Pd-PPh₂-PMO(Ph and Ph₂) nanomaterials and the results of water-medium reactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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