

Preparation of recyclable Pd(II) organometal catalyst with bicontinuous cubic Ia3d mesostructure for water-medium organic reaction

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Abstract: A heterogenous Pd(II) organometal catalyst with bicontinuous cubic Ia3d mesostructure was synthesized by surfactant-directed co-condensation of Pd [PPh₂(CH₂)₂Si(OCH₂CH₃)₃]₂Cl₂ and (CH₃CH₂O)₃SiPhSi(OCH₂CH₃)₃. In water-medium Sonogashira reaction ,the as-prepared Pd (II) -PMO-KIT-6 exhibited higher catalytic activity than reference catalyst Pd(II) -KIT-6 and could be used repetitively for more than 4 times ,which could reduce the cost and even diminish the environmental pollution from heavy metallic ions ,showing a good potential in industrial applications.

Key words: recyclable catalyst; Immobilization of Pd(II) organometal; bicontinuous cubic mesostructure; water-medium organic reactions

CLC number: O 643.32 **Document code:** A **Article ID:** 1000-5137(2012)06-0632-06

1 Introduction

Water is the most innocuous substance on Earth and thus ,the safest solvent possible. Sonogashira reactions have been widely used to organic synthesis^[1]. Due to solubility limit ,water-medium Sonogashira reaction has been mainly focused on homogeneous organometallic catalysts^[2]. Though highly active and selective ,the homogeneous catalysts are difficult for separation from the reaction system and thus ,could not be used repetitively ,leading to enhanced cost and even the environmental pollution from heavy metallic ions. Heterogeneous catalysts could overcome the above disadvantages but they usually exhibit much lower activity and selectivity than the corresponding homogeneous catalysts due to the poor distribution of active sites ,the steric hindrance and the alternation of the chemical environment^[3].

The three-dimensional (3-D) cubic mesoporous organosilica material designated PMO-KIT-6 is now attracting wide interest owing to the great perspectives of application in catalysis^[4]. On one hand ,the periodic mesoporous silicas (PMOs) with large surface area^[5] provide a promising way for designing immobilized homogeneous catalysts with high efficiency owing to the uniform distribution of active sites^[6]. Meanwhile ,

Received date: 2012-11-20

Foundation item: This work is supported by Natural Science Foundation of China (21107071 ,51273112) and Shanghai Government (10dj1400100 ,10PJ1408200 ,11YZ88 ,12CG52 and ssd10014) ,Shanghai Key Laboratory of Rare Earth Functional Materials.

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functionalization with organic groups was also performed to enhance surface hydrophobicity, which promoted the diffusion and adsorption of organic molecules on the catalysts, especially in aqueous medium^[7]. On the other hand, this unique 3-D interconnected network of PMO-KIT-6 provides an easy and direct access for organic molecules and facilitates inclusion or diffusion throughout the pore system without pore blockage. However, to our best knowledge, this 3-D mesoporous organometalsilica with both the organometal and organic fragments incorporated into silica framework has never been reported so far. Herein, we report the synthesis of a 3-D mesoporous organopalladium(II) silica catalyst with both Pd(II) organometals and phenyl groups (Ph) integrally incorporated into silica framework. This catalyst exhibits higher activity than the corresponding Pd(II) homogeneous catalyst and could be used repetitively, showing a good potential in industrial applications.

2 Experimental

2.1 Catalyst preparation

Firstly, the organometallicsilane Pd[PPh₂(CH₂)₂Si(OCH₂CH₃)₃]₂Cl₂ was synthesized by mixing 10 mL of toluene, 1.0 g of Pd(COD)Cl₂ and 2.7 g of PPh₂CH₂CH₂Si(OCH₂CH₃)₃ under argon atmosphere, followed by stirring at 25°C for 2 h. After being concentrated to 5.0 mL, pentane was added, leading to Pd[PPh₂(CH₂)₂Si(OCH₂CH₃)₃]₂Cl₂.

The periodic mesoporous organopalladium(II) silica, denoted as Pd(II)-PMO-KIT-6, was prepared by co-condensation method. In a typical synthesis, 1.2 g of P123 was dissolved in 40 g of distilled water and 3.0 g of 2.0 M HCl solution at 35°C. After complete dissolution, 1.1 g of butanol was added. After stirring for 1 h, 1.1 g of (CH₃CH₂O)₃SiPhSi(OCH₂CH₃)₃ (BTEB) was added to the solution. After being prehydrolyzed for 1 h, 0.21 g of Pd[PPh₂(CH₂)₂Si(OCH₂CH₃)₃]₂Cl₂ was added. This mixture was left under vigorous stirring at 35°C for 24 h. Subsequently, hydrothermal treatment of the reactant mixture was carried out at 100°C for 72 h under static conditions in a closed polypropylene bottle. Finally, the surfactants and other organic substances were extracted by refluxing in ethanol solution at 80°C for 24 h. The Pd(II) loading was determined as 1.2 wt% by ICP analysis.

For comparison, the Pd(II)-KIT-6 was also prepared. Briefly, 1.0 g of P123 was dissolved in 37 g of distilled water, 2.6 g of 35% HCl and 1.0 g of butanol under stirring at 35°C. Then 2.1 g of TEOS was added. After being prehydrolyzed for 1 h, 0.21 g Pd[PPh₂(CH₂)₂Si(OCH₂CH₃)₃]₂Cl₂ was added into the solution. The mixture was left under stirring for 24 h at 35°C, and subsequently heated for another 24 h at 100°C under static conditions in a closed polypropylene bottle. The yellow solid product was collected and the surfactants extracted. The Pd(II) loading was determined as 0.99 wt% by ICP analysis.

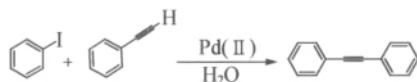
2.2 Characterization

Structural characteristics were characterized by X-ray diffraction (XRD, Rigaku D/max-RB CuKα), transmission electron microscopy (TEM, JEOL JEM2100), and N₂ adsorption-desorption isotherms (Quantachrome NOVA 4000e) and solid state nuclear magnetic resonance (NMR, Bruker AV-400). Specific surface areas (*S*_{BET}), average pore diameter (*D*_p) and total pore volume (*V*_p) 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 $C_{1s} = 284.6$ eV as a reference. The metal loadings were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, Varian VISTA-MPX).

2.3 Activity test

Sonogashira reaction (Scheme 1) was used as probe to evaluate the catalytic performances, which was conducted in a 10 mL round-bottomed flask at 80°C under vigorous stirring. In a typical run of the reaction, 0.50 mmol iodobenzene, 0.60 mmol phenylacetylene, 0.20 mL 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU), 4.0 mL H_2O , *n*-decane as an internal standard and a catalyst containing 0.0060 mmol Pd(II) were mixed in the flask and allowed to react for 5 h. Then the products were extracted by acetic ether, followed by analysis on a gas chromatograph (SHIMADZU, GC-17A) equipped with a JWDB-5 95% dimethyl 1-(5%) -diphenylpolysiloxane column and a FID detector.



Scheme 1 Sonogashira reaction between iodobenzene and phenylacetylene

In order to determine durability, the catalyst was allowed to centrifuge after each run of reactions and the clear supernatant liquid was decanted slowly. The catalyst was washed thoroughly with distilled water and ethanol, followed by drying at 80°C under vacuum condition. Then, the catalyst was reused with fresh charge of reactants for subsequent recycle under the identical reaction conditions.

3 Results and discussion

3.1 Structural characteristics

As shown in Fig. 1, the ^{29}Si MAS NMR spectrum revealed that the Pd(II)-PMO-KIT-6 displayed three peaks down-field corresponding to T^1 ($\Delta = -63$ ppm), T^2 ($\Delta = -73$ ppm) and T^3 ($\Delta = -81$ ppm), where $T^m = \text{RSi}(\text{OSi})_m - (\text{OH})_{3-m}$, $m = 1 \sim 3$. No Q^n peaks were observed, where $Q^n = \text{Si}(\text{OSi})_n - (\text{OH})_{4-n}$, $n = 2 \sim 4$ indicating that all the Si species were covalently bonded with carbon atoms^[8]. Meanwhile, two peaks around 1.5×10^{-5} and 3.2×10^{-5} were observed in the ^{13}C CP MAS NMR spectrum, which could be assigned to two C atoms in the $-\text{CH}_2-\text{CH}_2-$ group connecting with the PPh_2 -group. An intense peak around 1.31×10^{-4} could be attributable to the C atoms in the benzene ring (Ph). A weak peak around 5.9×10^{-5} was assigned to the C atoms in the $\text{C}_2\text{H}_5\text{O}$ -group connecting with silicon due to the incomplete hydrolysis^[9]. Other peaks denoted by asterisks were attributed to spinning sidebands, as verified by changing rotating speeds^[10]. In addition, the ^{31}P CPMAS NMR spectrum showed a single signal at 3.9×10^{-5} , corresponding to P atom in the PPh_2 -groups. The other peaks could be assigned to rotation side bands since their positions changed with the spinning speed. These results clearly demonstrated the integral incorporation of both the Pd(II) organometal and the Ph group into the silica framework.

As shown in Fig. 2(a), the XPS spectra demonstrated that all the Pd species in the Pd(II)-PMO-KIT-6

were present in +2 oxidation state, corresponding to the binding energy around 343.3 eV in Pd_{3d5/2} level, which further confirmed the sole coordination model between the Pd(II) ion and the PPh₂-ligand. In comparison with free Pd(PPh₃)₂Cl₂, the Pd(II) binding energy in the Pd(II)-PMO-KIT-6 shifted negatively by 1.3 eV, possibly due to the stronger electron-donating ability of P in the PPh₂(CH₂CH₂) than that in the PPh₃, taking into account that π conjugated system between P and three phenyl groups could dilute the electron density on the P atom.

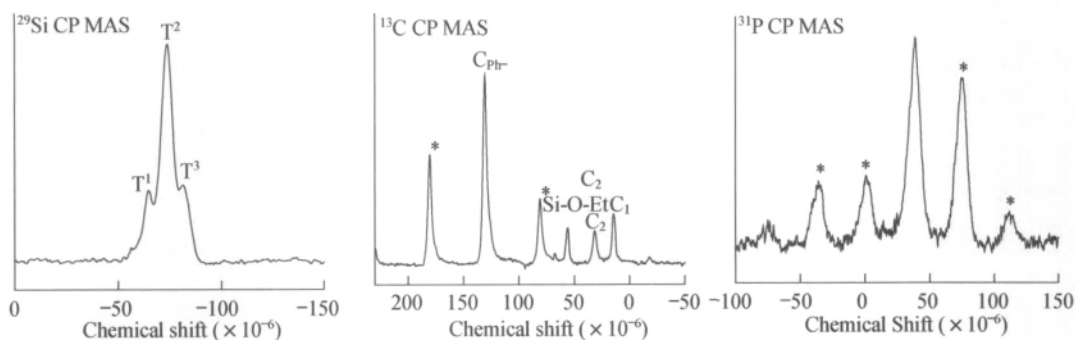


Figure 1 NMR spectra of the Pd(II)-PMO-KIT-6 sample

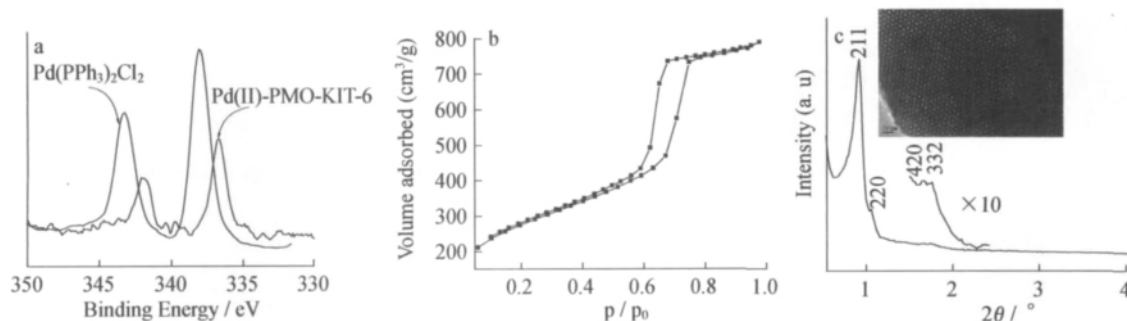


Figure 2 XPS spectra of different samples (a), N₂ adsorption-desorption isotherms (b) and XRD pattern (c) of the Pd(II)-PMO-KIT-6 sample (The inset is the TEM image)

Fig. 2 (b) revealed that the Pd(II)-PMO-KIT-6 displayed a typical IV type N₂ adsorption-desorption isotherm with a H₁ hysteresis loop indicative of the mesoporous structure. The low-angle XRD pattern in Fig. 2 (c) showed an intense peak around $2\theta = 0.90^\circ$ indicative of (211) and (220) diffraction and three additional weak peaks at higher 2θ values corresponding to (220), (420) and (332) diffractions. These results demonstrated that the Pd(II)-PMO-KIT-6 contained ordered 3-dimensional mesoporous channels^[9], which was further confirmed by TEM images. Some structural parameters including surface area (S_{BET}), pore diameter (D_p) and pore volume (V_p) were summarized in Table 1.

3.2 Catalytic performances

Table 1 summarized the catalytic parameters of various catalysts in Sonogashira reaction conducted in aqueous media. As revealed in Table 1, Pd(II)-PMO-KIT-6 exhibited much higher activity than Pd(II)-KIT-6 in water-medium Sonogashira reaction with the same amount of Pd(II) used. One possible reason was that

the presence of phenyl groups in the silica walls might enhance the surface hydrophobicity of the catalyst, which facilitated the diffusion and adsorption of organic reactants, especially in water medium. Meanwhile, no significant decrease in catalytic efficiencies was observed for the Pd(II)-PMO-KIT-6 catalyst within 4 recycles exhibiting excellent durability. This could be attributed to the strong interaction of the Pd(II) organometallic complex with the organosilica support, which could effectively inhibit the Pd(II) leaching. According to the ICP analysis, Pd(II) species in the solution was less than 0.5×10^{-7} after being used for 4 times, suggesting that the Pd(II) leaching could be essentially neglected.

Table 1 Structural parameters and catalytic performances of different catalysts of different catalysts^a

Catalyst	$S_{BET}/(\text{m}^2 \cdot \text{g}^{-1})$	$V_p/(\text{cm}^3 \cdot \text{g}^{-1})$	D_p/nm	Pd loading/%	Conv/%	Yield/%
Pd(II)-KIT-6	695	0.80	5.3	1.1	89	89
Pd(II)-PMO-KIT-6	893	1.2	6.8	1.4	96	96
Pd(II)-PMO-KIT-6 ^b	686	1.0	6.2	1.3	84	84

^a See reaction conditions in activity test section; ^b After being used for 3 times.

4 Conclusions

In summary, this work developed a facile approach to synthesize a 3-D periodic mesoporous Pd(II) organometal-silica catalyst with both the Pd(II) organometals and phenyl groups incorporated into the silica walls. During water-medium Sonogashira reactions, the Pd(II)-PMO-KIT-6 exhibited higher activity than the Pd(II)-KIT-6. Remarkably, Pd(II)-PMO-KIT-6 could be used repetitively for more than 4 times without significant deactivation, which offered opportunities for industrial applications of water medium clean organic reactions.

References:

- [1] ROUSH W R. Comprehensive Organic Synthesis[M]. New York: Pergamon Press, 1991.
- [2] NARAYAN S, MULDOON J, FINN M G, et al. On "water": unique reactivity of organic compounds in aqueous suspension [J]. *Angewandte Chemie International Edition* 2005, 44(22): 3275–3279.
- [3] LU Z, LINDNER E, MAYER H A. Applications of sol-gel-processed interphase catalysts [J]. *Chemical Reviews* 2002, 102(10): 3543–3578.
- [4] GUO W P, KLEITZ F, CHOAB K, et al. Large pore phenylene-bridged mesoporous organosilica with bicontinuous cubic Ia3d [combining macron] (KIT-6) mesostructure [J]. *Journal of Material Chemistry* 2010, 20(38): 8257–8265.
- [5] TAN X H, SHEN B, DENG W, et al. Novel carbonyl allylation mediated by $\text{SnCl}_2/\text{TiCl}_3$ in water [J]. *Journal of Organic Letters* 2003, 5(11): 1833–1835.
- [6] WAN Y, ZHANG D Q, FENG C M, et al. Periodic mesoporous organosilicas: a type of hybrid support for water-mediated reactions [J]. *Chemistry—An Asian Journal* 2007, 2(7): 875–881.
- [7] LI H X, ZHANG F, YIN H, et al. Water-medium isomerization of homoallylic alcohol over a Ru(II) organometallic complex immobilized on FDU-12 support [J]. *Green Chemistry* 2007, 9(5): 500–505.

- [8] BUELEIGH M, MICHAEL A, MARKOWITZ M, et al. Direct synthesis of periodic mesoporous organosilicas: functional incorporation by co-condensation with organosilanes [J]. *Journal of Physical Chemistry B* 2001, 105(41): 9935 - 9942.
- [9] INAGAKI S, GUAN S, OHSUNA T, et al. An ordered mesoporous organosilica hybrid material with a crystal-like wall structure [J]. *Nature* 2002, 416(6878): 304 - 307.
- [10] SIMON P F W, ULRICH R, SPIESS H W, et al. Block copolymer-ceramic hybrid materials from organically modified ceramic precursors [J]. *Chemical of Materials* 2001, 13(10): 3464 - 3486.

周期有序双连续介孔结构 Pd(II) 有机金属催化剂 用于水介质 Sonogashira 反应的研究

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摘 要: 以 1,4-双(三乙氧基硅基)苯和苯基膦钯有机金属硅烷为混合硅源,在表面活性剂导向组装下共缩聚制得 Pd(II)-PMO-KIT-6 非均相催化剂,并利用 NMR、XPS、XRD、TEM 和氮气吸附等手段对催化剂进行了表征。考察了该催化剂在水介质 Sonogashira 反应中的催化性能。结果表明:所制备的 Pd(II)-PMO-KIT-6 具有优异的催化活性和选择性,这主要归因于催化剂的高比表面积、双连续介孔结构有利于提高 Pd(II) 活性位分散度,减少传质阻力;同时苯基桥联 PMO 构建形成的微环境增强表面疏水性,有利于反应底物的吸附和扩散。此外,催化剂还可以重复使用多次后活性没有明显降低。

关键词: 非均相催化; 双连续介孔结构; 有机金属固载化; 水介质清洁有机合成

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