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β -Diketimine appended periodic mesoporous organosilica as a scaffold for immobilization of palladium acetate: An efficient green catalyst for Wacker type reaction

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ABSTRACT

A series of β -diketimine appended periodic mesoporous organosilicas (PMOs) were prepared and characterized. These PMOs were found to be an excellent scaffold for the immobilization of palladium acetate [Pd(OAc)₂] through the complexation between Pd(OAc)₂ and iminic nitrogen atoms of β -diketiminate, leading to the formation of efficient heterogeneous catalysts (Pd/PMOs) for the oxidation of styrene. Catalytic evaluations show that, in liquid phase using H₂O₂ as oxidant, Pd/PMOs could promote styrene to undergo Wacker type reaction with a high selectivity of up to 100% toward the formation of acetophenone, a useful chemical with high demand in the global market. The novel solid catalyst offers a good catalytic recyclability with consistently high catalytic activity. In addition, it was experimentally demonstrated that H₂O₂ plays an important role to prevent unwanted catalyst deactivation. Thus, the current work presents a convenient approach for the direct production of acetophenone from styrene.

1. Introduction

In 1999, seven years after Mobil reported MCM 41-type mesoporous silica materials [1], researchers have developed a novel concept to prepare mesoporous materials in which an organosilane containing at least two terminal trialkoxysilane groups was used as a silica source to form organic/inorganic hybrid materials, termed as periodic mesoporous organosilica (PMO) [2–4]. The presence of organic functionality within the inorganic silica framework not only provides the robustness to the structure, but also makes PMO potentially useful for various applications. Designing catalytically active PMO, one of the most important applications, is a novel strategy for transforming a catalytically important transition metal complex into a heterogeneous catalyst [5–9].

In the current research, we synthesized a new type of PMO immobilized with β -diketimine moiety bound onto the framework walls through a distribution at molecular level. β -Diketimine has gained a lot of attention as a versatile ligand for the formations of various transition metal complexes that have been proven to be useful in catalysis, metallo-organic chemical vapor deposition,

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and so on [10–14]. For instance, Jin *et. al.* have reported air and moisture stable β -diketiminato-Pd complex for catalytic C-C coupling reactions [12–14]. In this work, we capitalized the embedded β -diketiminate centers in PMO to coordinate with Pd(OAc)₂, leading to a heterogeneous architecture consisting of stable PMO immobilized with β -diketiminato-acetate Pd²⁺ complex for catalytic applications.

In the area of catalysis, one of the important research directions is the direct and selective oxidation of various hydrocarbons on account of their industrial as well as academic significance. Among various commercially imperative oxidation processes, Wacker reaction is always a popular topic especially in the functionalization of terminal olefins [15-17]. An excellent representation of Wacker reaction is the selective oxidation of styrene to acetophenone, an important raw material in petrochemical, pharmaceuticals, resin, and fragrance industries [18]. A commonly utilized industrial process for the production of acetophenone is the acetylation of benzene using acetyl chloride/acetic anhydride, which is considered as an inefficient process [19]. On the contrary, Pd catalyzed Wacker reaction is a clean process to produce acetophenone as compared to the Friedel-Crafts route. However, Wacker reaction for the styrene oxidation is often associated with various problems, such as low selectivity toward the acetophenone production, difficulties in the product separation, uses of acetic acid and CuCl₂ to promote the reoxidation of Pd(0) into highly active Pd(II) resulting





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in the corrosion hazards of the reactor, and generation of large amounts of toxic and corrosive wastes [20]. In order to circumvent these major drawbacks associated with the Wacker process, many catalytic systems have been investigated for the selective oxidation of styrene to acetophenone. Hitherto, improved efficiency of the catalytic systems has been attempted by avoiding copper(II) salts [20], using supported catalysts [21–23], surfactants [24], cyclodextrins [25], and calixarenes [25]. In addition, making use of various alternative solvents such as fluorous phase [26], polyethylene glycols [27], supercritical CO₂ [21,28], and ionic liquids [19,29] have been adopted to reduce the main drawbacks of the Wacker oxidation process. However, the development of a simple, efficient, and environmentally benign method for selective synthesis of styrene to acetophenone is still of great challenge.

In order to address the challenge, herein, we developed a novel strategy to immobilize $Pd(OAc)_2$ onto the PMO frameworks via the formation of β -diketiminato-acetate Pd^{2+} complex. Heterogeneous catalysis of the styrene oxidation in liquid phase using PMO based catalysts have been studied in few instances, where epoxide and benzaldehyde were formed as selective products [30–33]. To our best knowledge, this is the first demonstration of employing PMO based catalytic system for selective oxidation of styrene to acetophenone through Wacker reaction using H_2O_2 as oxidant. In the present work, various control reactions were carried out in order to establish a green catalytic process in terms of high selectivity as well as high catalyst reusability.

2. Experimental

All the chemicals and materials used in the synthesis and catalysis were purchased from Sigma-Aldrich or Alfa Aesar and used without further purifications.

2.1. Synthesis of β -diketimine (1)

β-Diketimine (1) was synthesized according to a reported method with some modifications [12]. In a typical synthesis (Scheme 1), acetylacetone (1.0 g, 10 mmol) and 4-aminophenol (2.2 g, 20 mmol) were dissolved in absolute ethanol (50 mL) in a round bottom flask (100 mL) containing a magnetic stir bar. Conc. HCl (0.5 g) was added into the mixture solution. After the reaction mixture was refluxed for 3 days, the mixture was cooled down to room temperature and treated with water (20 mL) containing Na₂CO₃. The solution was extracted with dichloromethane for three times (20 mL each). The organic layer was dried through MgSO₄ and then concentrated under reduced pressure. The solid product was washed with cold ethanol and dried under vacuum to give compound **1**. Product yield 34%. ¹H NMR (CD₃OD, 300 MHz, ppm) δ 7.30 (d, 4H, *J* = 9 MHz), 6.72 (d, 4H, *J* = 9 MHz), 2.08 (s, 6H), 1.29 (s, 2H); ¹³C NMR (400 MHz, CDCl₃, ppm) δ 158.9, 153.4, 142.3, 121.2, 118.6, 40.0, 23.2; IR: v 3430, 3062, 2852, 1680, 1610, 1594 cm⁻¹; MS: calcd for C₁₇H₁₈N₂O₂ *m*/*z* = 282, found: *m*/*z* = 282. Elemental analysis: calcd%: C 72.32, H 6.43, N 9.92, found%: C 72.88, H 6.08, N 10.1.

2.2. Synthesis of β -diketiminato bis(4,1-phenylene) bis(3-triethoxysily|propylcarbamate) (**2**)

In a typical synthesis of compound **2** (Scheme 1), synthesized compound 1 (1.0 g, 3.5 mmol) was dissolved in dry THF (50 mL) under N₂ in a two-necked round bottom flask equipped with a condenser. 3-Isocyanatopropyltriethoxysilane (1.8 g, 7.0 mmol) was then added dropwise to the solution over 30 min. After the reaction mixture was refluxed for 24 h, it was cooled down to room temperature. THF was removed in vacuo, leaving a highly viscous liquid. Hexane was added to the viscous liquid, and the precipitates were formed to afford compound 2. Product yield 80%. ¹H NMR (CD₃OD, 400 MHz, ppm) δ 7.54 (d, 4H, J = 8 MHz), 7.04 (d, 4H, *J* = 12 MHz), 3.84 (q, 12H, *J* = 8 MHz), 3.16 (t, 4H, *J* = 8 MHz), 2.11 (s, 6H), 1.64 (s, 2H), 1.22 (t, 18H, J=8 MHz), 0.66 (t, 4H, J = 8 MHz); ¹³C NMR (400 MHz, CDCl₃, ppm) δ 159.4, 151.8 149.4, 144.2, 124.2, 121.0, 57.8, 45.0, 40.2, 24.8, 22.9, 18.4, 11.2; IR: v 3323, 2976–2887, 1714, 1670, 1551, 1506, 1207, 1082 cm⁻¹; MS: calcd for $C_{37}H_{60}N_4O_{10}Si_2$ m/z = 777, found: m/z = 778 (MH⁺). Elemental analysis: calcd%: C 57.19, H 7.78, N 7.21, found%: C 57.01, H 8.19. N 7.43.

2.3. Synthesis of PMOs by hydrothermal process

PMO was prepared according to a reported method with some modifications [8]. Compound **2** and tetraethylorthosilicate (TEOS) were used as silica sources, and cetyltrimethylammonium bromide (CTAB) was used as the structure-directing agent. A gel was formed with a particular molar ratio of Si: CTAB: NH₃ (25%): H₂O: EtOH = 1.0: 0.12: 8.0: 114: 10. Three different molar ratios of **2** to TEOS including 2%, 5%, and 10% were used, leading to PMO-1,



Scheme 1. Schematic representation for the synthesis for compounds 1 and 2.

PMO-2, and PMO-3, respectively. In a typical synthesis of PMO with 2% of **2**, CTAB (1.5 g, 4.1 mmol) was dissolved in H₂O (70 mL), and then NH₃ solution (20 mL of 25% NH₃ solution, 0.9 g mL⁻¹, 265 mmol) was added. The mixture solution was stirred at 40 °C for 30 min to give a clear solution. A premixed solution of **2** (0.5 g, 0.6 mmol) and TEOS (5.8 g, 28.0 mmol) in EtOH (18 mL) was added to the above solution under vigorous stirring. After 2 h, the resulted gel was transferred to a polyethylene container, which was then heated to 90 °C for 4 days. The solid obtained was washed with H₂O and dried in air at 60 °C. The structure-directing agent was finally removed by extraction of the solid with dilute ethanolic HCl solution (20 mL of 0.5 M ethanolic HCl for 0.5 g of solid) at 40 °C for 2 h. PMO was obtained by filtration and then dried in vacuo.

2.4. Synthesis of PMOs containing Pd complex (Pd/PMO-n)

In a typical synthesis of Pd/PMO, Pd(OAc)₂ (23 mg, 0.1 mmol) was dissolved in dry dichloromethane (10 mL) and then PMO-n (200 mg) was added. The mixture was stirred at room temperature for 24 h. The resulted solid was isolated by centrifugation and washed with dichloromethane using Soxhlet extraction for another 24 h. The solid was then dried at 80 °C under vacuum for 12 h to yield a brown powder. After the incorporation of Pd(OAc)₂ into PMO-1, PMO-2, and PMO-3, the resulted materials were denoted as Pd/PMO-1, Pd/PMO-2, and Pd/PMO-3, respectively.

2.5. Catalytic tests

The catalytic tests were carried out in a two-necked round bottom flask. In a typical experiment, styrene (1.0 g, 10 mmol) was added to an acetonitrile solution (30 mL) containing Pd/ PMO-n as catalyst. In order to avoid immediate decomposition of H₂O₂ and its strong effervescence, 30% H₂O₂ (3.4 g, 30 mmol) was added slowly to the mixture solution over a period of 3 h. The resulting mixture was stirred under 400 rpm at 60 °C for 5 h. The product was analyzed qualitatively using gas chromatographymass spectrometry (GC-MS). Then, the solvent from the reaction mixture was evaporated under vacuum, and the crude product was purified by column chromatograph using silica gel with *n*-hexane/ethyl acetate (v/v 5:1) as eluent. The acetophenone product was obtained as a colorless liquid. Isolated product was also weighed to validate the GC-MS result and further characterized by MS and NMR. A similar procedure was adopted to carry out the catalysis using Pd(OAc)₂ and β -diketiminato-acetate Pd²⁺ complex (L-Pd(OAc)₂) as the catalyst (see the Section S8 in the Supporting Information (SI) for more details).

In order to examine the recyclability of the Pd/PMO catalyst, the catalyst from the reaction mixture was recovered by centrifugation followed by washing with acetonitrile for several times. The recovered catalyst was kept under vacuum oven for complete dryness before using for the subsequent catalysis or various characterizations.

2.6. Characterizations

¹H NMR spectra were recorded on a Bruker spectrometer operating at 400 MHz. The solid-state NMR spectra were performed on an ECA400 NMR spectrometer (JEOL, 400 MHz) using a 4 mm CP/MAS probe at room temperature. Scanning was carried out with spinning rate of 10000 Hz and 5000 scans. Transmission electron microscopy (TEM) images were collected on a JEOL JEM-1400 instrument operated at 100 kV. FT-IR spectra were recorded as KBr pellets on a SHIMADZU IRPrestige-21 spectrometer with the sample powder diluted in KBr (1%). N₂ adsorption/desorption measurements for Brunauer–Emmett–Teller (BET) and non-local density functional theory (NLDFT) calculations were performed

using an autosorp-IQ instrument from Quantachrome Instruments Corporation. The BET method was utilized to calculate the specific surface areas of the PMO materials, whereas the NLDFT equilibrium model for cylindrical pores considering N₂ as adsorbate and silica as adsorbent at 77 K was adopted for measuring the pore size distributions of the PMOs. Elemental analyses (EA) were obtained from EuroVector Euro EA Elemental Analyzer. Thermo Fischer iCAP 6000 series inductively coupled plasma-atomic emission spectroscopy (ICP-OES) was used for performing trace metal analysis. X-ray photoelectron spectroscopy (XPS) analysis was carried out by a SPECS HSA3500 plus spectrometer using Mg X-ray source. Quadrupole ion trap mass spectrometer equipped with Thermo Finnigan Trace GC ultra was used for the identification of various products from the catalytic reactions.

3. Results and discussion

3.1. Synthesis of organo alkoxysilane

PMO is a unique hybrid material with a uniform molecular distribution of organic bridging units within inorganic silica network. In the current work, an essential organic precursor with two terminal alkoxysilanes, compound 2, was synthesized through two-step reactions (Scheme 1). Throughout the synthesis including the isolation and storage of compound 2, moisture free and inert conditions were adopted in order to avoid unwanted polymerization of silane. Compound 2 was characterized by common analytical tools as mentioned in the experimental section. The FT-IR spectrum (Fig. S2 in the SI) of compound 2 shows characteristic signals attributed from C=O (1714 cm⁻¹), N-H (3323 and 1670 cm⁻¹), C=N (1551 cm⁻¹), C-N (1506 cm⁻¹), Si-C (1207 cm⁻¹), Si-O (1082 cm⁻¹), and C–H (2976–2887 cm⁻¹) vibrations, which provides solid evidence for the successful formation of compound 2. The ¹H NMR (Fig. S6 in the SI) and ¹³C NMR (Fig. 2a) spectra were also obtained to characterize the compound.

3.2. Synthesis and characterization of β -diketiminate incorporated PMOs

3.2.1. FT-IR study of PMOs

The FT-IR spectra (Fig. 1) of PMO-1, PMO-2, and PMO-3 show characteristic peaks of typical siloxane network in mesoporous silica materials [34,35]. The peaks in the range from 1550 to 1400 cm^{-1} (inset in Fig. 1) in all the three FT-IR spectra are assigned to the organic unit in compound **2**, providing clear evidence of immobilized compound **2** into the organosilica framework. It can also been seen from the spectra that the intensities of the peaks attributed by **2** gradually increased upon the loading amount increase of compound **2** during the preparation. The predominant band of physisorbed water centered at 1630 cm⁻¹ overlaps completely with the peaks of the C=O and C=N bonds, while the signals attributed by the C=N, C–NH, and C–O bonds could be observed in the spectra (inset in Fig. 1). A broad band around 3426 cm⁻¹ is attributed to the O–H stretching vibration of hydrogen bonded silanols on PMOs [36].

3.2.2. ¹³C and ²⁹Si solid-state NMR study of PMOs

The 13 C cross-polarization magic angle spinning (CP MAS) NMR spectra of PMO-1, PMO-2, and PMO-3 (Fig. 2) exhibit strong signals ranging from 9 to 42 ppm, which can be attributed to different aliphatic primary and secondary carbon atoms from the organic bridging unit. Strong signals from aromatic carbons on the phenyl ring can be identified at ~105 ppm as well as in the range from 140 to 150 ppm. In addition to these signals, two significant peaks at 151 and 157 ppm are assigned to the carbons from carbamate



Fig. 1. FT-IR spectra of (a) PMO-1, (b) PMO-2, (c) PMO-3, and (d) compound 2.



Fig. 2. ¹³C NMR spectrum of (a) compound 2 and ¹³C CP MAS NMR spectra of (b) PMO-1, (c) PMO-2, and (d) PMO-3.

and imine groups of the incorporated organic bridging unit, respectively. Since these signals can be easily correlated with the ¹³C NMR spectrum of compound **2** (Fig. 2a), the CP MAS NMR data provide a solid support for the successful incorporation of compound 2 into the silica framework in the synthesized PMOs. ²⁹Si CP MAS NMR analysis was also carried out for all the three PMOs in order to realize the covalent incorporation of the organic bridging units into the siloxane network.²⁹Si NMR spectra of PMO-1, PMO-2, and PMO-3 (Fig. 3) show the signals with major intensities centered at -110 and -100 ppm and a small shoulder at -90 ppm, which can be assigned to Q^4 [(\equiv SiO)₄Si], Q^3 [(\equiv SiO)₃Si(OR)], and Q^2 [(\equiv SiO)₃Si(OR)₂], respectively, where R = Et or H. Along with these signals, all the spectra displayed one more peak at -67 ppm, corresponding to T resonance from silicon species attached to the organic group. ²⁹Si CP MAS NMR spectra also provide solid evidence in support of complete immobilization of



Fig. 3. ²⁹Si CP MAS NMR spectra of (a) PMO-1, (b) PMO-2, and (c) PMO-3.

organic bridging unit into the silica framework through the hydrolysis of terminal alkoxysilanes.

3.2.3. Isothermal N₂ adsorption/desorption measurements of PMOs

The isothermal N₂ adsorption/desorption measurements were carried out for the three PMOs to determine their surface areas and pore size distributions (Figs. S7 and S8 in the SI). From the N₂ adsorption isotherm under the lowest pressure, the BET surface areas of PMO-1, PMO-2, and PMO-3 were measured to be 720, 676, and 712 m² g⁻¹, respectively (Table 1). The NLDFT equilibrium

 Table 1

 BET surface area and NLDFT pore diameter of PMOs.

No	Materials	BET surface area $(m^2 g^{-1})$	NLDFT pore diameter (nm)		
1	PMO-1	720	2.9		
2	PMO-2	676	3.0		
3	PMO-3	713	3.7		

model for the pore size distributions indicates the presence of mesopores in all the PMOs, and the average pore diameters for PMO-1, PMO-2, and PMO-3 were found to be 2.9, 3.0, and 3.7 nm, respectively (Table 1). A profound effect was observed between the loading percentages of compound **2** and the mesopore size, which can be attributed to the swelling of the pore channels caused by the addition of organic bridging unit with high degree of complexity.

3.2.4. Mesostructural morphology of PMOs

TEM analysis (Fig. 4a–c) shows mesostructural morphologies for PMO-1, PMO-2, and PMO-3, which are in accordance with the NLDFT calculation from N_2 adsorption/desorption measurements. PMO-1 and PMO-2 exhibit the presence of regular mesoporous channels. However, the periodicity of the mesoporous channels gradually declines upon increasing the loading percentage of organic unit, which becomes significant in the case of PMO-3.

3.3. Synthesis and characterization of Pd/PMOs

The incorporation of $Pd(OAc)_2$ into PMOs was achieved by generating β -diketiminato-acetate Pd^{2+} complex through a method

discussed in the experimental section (Scheme 2). The Soxhlet extraction method was adopted to ensure the removal of free Pd²⁺ from the materials, leaving behind only the Pd²⁺ immobilized PMOs. Successful incorporation of Pd²⁺ was confirmed quantitatively through the ICP analysis for each Pd/PMO, and the obtained results show that the Pd contents in Pd/PMO-1, Pd/PMO-2, and Pd/PMO-3 are 0.13, 0.16, and 0.24 mmol g⁻¹, respectively (Table 2). From EA, it was found that the amount of β-diketiminato unit in each Pd/PMO is almost equal to the Pd content in the Pd/PMO, indicating the 1:1 coordination between them (Table 2).

3.3.1. TEM study of Pd/PMOs

The TEM images (Fig. 4d–f) show the retention of the mesostructural morphologies for Pd/PMO-1, Pd/PMO-2, and Pd/PMO-3, which are apparently similar to that of PMO-1, PMO-2, and PMO-3, respectively. The observations indicate that the synthesized PMOs possess enough structural stability in order to maintain their morphological integrity even after the metal incorporation. In many previous reports where Pd(OAc)₂ was attempted to load into porous materials, black dots were observed in the TEM images of obtained materials, which may be attributed



Fig. 4. TEM images of (a) PMO-1, (b) PMO-2, (c) PMO-3, (d) Pd/PMO-1, (e) Pd/PMO-2, and (f) Pd/PMO-3.



Scheme 2. Schematic representation for the incorporation of Pd(OAc)₂ into the PMOs.

Table 2

Analytical, textural, and porosity data of different Pd/PMO catalysts.

No	Catalyst	CHN analysis (wt%)		S	Amount of β -diketiminato (mmol g ⁻¹)	Pd content from ICP $(\text{mmol } \text{g}^{-1})$		N_2 adsorption/desorption measurements	
		С	Ν	Н		Before catalysis	After catalysis	BET surface area (m ² g ⁻¹)	NLDFT pore diameter (nm)
1	Pd/PMO- 1	3.66	0.89	3.02	0.159	0.133	0.131 ^a	655	2.65
2	Pd/PMO- 2	5.84	1.00	2.52	0.179	0.159	0.157 ^a	625	2.77
3	- Pd/PMO- 3	6.74	1.43	3.21	0.25	0.238	0.232 ^b	570	3.18

^a Catalyst recovered from single catalytic cycle.

^b Catalyst recovered from the 5th catalytic cycle.

to the formation of Pd(0) nanoparticles [37–40]. The formation of the nanoparticles has been described as an outcome of electronbeam induced reduction of original Pd(II) species during the TEM measurements [40]. In our Pd-loaded PMOs, however, there was no evidence for the formation of Pd nanoparticles on PMOs, which endorses the molecular distribution of β -diketiminato-acetate Pd²⁺ complex into PMOs.

3.3.2. Isothermal N_2 adsorption/desorption measurements of Pd/PMOs A significant reduction in the BET surface area was observed for all Pd/PMOs upon the incorporation of Pd(OAc)₂ (Table 2 and Fig. 9 in the SI). This change can be ascribed to the fact that incorporated Pd(OAc)₂ occupies certain amount of space inside the pores, resulting in a contraction of the pore diameter. The decrease in the average pore diameter of Pd/PMOs after the introduction of Pd²⁺ is also evidenced from the NLDFT average pore size distribu-

3.3.3. FT-IR study of Pd/PMOs

tion analysis (Table 2 and Fig. S10 in the SI).

The FTIR spectra (Fig. 5) of Pd/PMO-1, Pd/PMO-2, and Pd/PMO-3 show all the characteristic peaks of PMOs as well as the peaks of acetate groups from Pd(OAc)₂. These IR signals provide solid evidence in support of the formation of β -diketiminato-acetate Pd²⁺ complex within Pd/PMOs. The intensities of the peaks contributed by the acetate groups increase as a direct function of the loading amount of compound **2** in PMOs. This is an obvious phenomenon, since the more β -diketimine units are incorporated within PMOs, the more β -diketiminato-acetate Pd²⁺ complex is formed.

3.3.4. XPS study of Pd/PMOs

The incorporation of Pd²⁺ into PMOs through the complexation with the iminic nitrogen atoms of the β -diketiminate moiety was further investigated by high resolution XPS. The XPS spectra of

Pd/PMO-1, Pd/PMO-2, and Pd/PMO-3 are presented in Figs. S11– S13 in the SI. The high resolution XPS spectra of Pd/PMO-1, Pd/ PMO-2, and Pd/PMO-3 (Fig. 6) exhibit characteristic $3d_{5/2}$ peak with the binding energy (BE) of 337.8 eV, indicating the presence of Pd²⁺ in PMOs [41]. However, the BE value of the $3d_{5/2}$ peak in the cases of Pd/PMOs shows a decline as compared to that (338.7 eV) of Pd(OAc)₂. This negative shift in the BE value of $3d_{5/2}$ peak can be attributed to the strong coordination of Pd(OAc)₂ with the iminic nitrogen atoms of the β -diketiminate moiety, which eventually makes the Pd²⁺ species less electron deficient. On account of this observation, a rational conclusion regarding the successful immobilization of β -diketiminato-acetate Pd²⁺ complex within Pd/PMOs can be reached.

3.4. Catalytic test

Catalytic activity of different Pd/PMO catalysts for the oxidation of styrene was evaluated at 60 °C using acetonitrile as solvent and H_2O_2 as oxidant. As seen from the results (Table 3), it is evident that all the Pd/PMOs offer nearly 100% selectivity toward the production of acetophenone, which is in contrast to many other reports where benzaldehyde was the predominant product by using Pd²⁺ as a catalyst without cocatalyst [22]. Among three Pd/ PMO catalysts, Pd/PMO-3 demonstrated the highest catalytic activity (Table 3, entry 4) under the given reaction conditions. Due to the low Pd loading in Pd/PMO-1 and Pd/PMO-2, the required amount of solid catalysts is much higher, making the catalyst-suspended reaction mixture very dense. Consequently, the mobility of the reaction substrate in solution is reduced markedly, which is difficult for the substrate to defuse effectively into the pore channels for reaction. Moreover, most of the substrate got adsorbed on the surface of Pd/PMOs and remained unreacted due to a low density of catalytic site on the surface of Pd/PMOs. These are the



Fig. 5. FT-IR spectra of (a) Pd/PMO-1, (b) Pd/PMO-2, (c) Pd/PMO-3, and (d) $Pd(OAc)_{2}$.



Fig. 6. High-resolution XPS spectra at the 3d region for (a) Pd/PMO-1, (b) Pd/PMO-2, (c) Pd/PMO-3, and (d) Pd(OAc)₂.

primary reasons responsible for low conversion and low TOF_A (turnover frequency) observed in the case of Pd/PMO-1 and Pd/ PMO-2. A series of reactions were carried out by varying the solvent volume, and a profound effect was observed (Fig. S14 in the SI). Poor catalytic activity was observed when the volume of



Fig. 7. Catalytic activities of Pd/PMO-3 in terms of styrene conversion and selectivity of different products as a function of reaction time. Reaction conditions: styrene/H₂O₂ = 1:3 (mole ratio), styrene/catalyst = 200:1 (mole ratio), 30 mL of acetonitrile as solvent at 60 °C.

solvent was as low as 20 mL, which can be improved by increasing the volume. However, a slight decrease of activity in the case of Pd/ PMO-3 was also observed upon the increase of solvent volume, mainly due to the high dilution effect. On the other hand, very poor conversion of styrene was observed in the absence of any Pd/PMO catalyst even after 12 h of reaction, resulting in preferential production of benzaldehyde and benzoic acid (Table 3, entry 1). The catalytic activity of prepared Pd/PMOs was also compared with their homogeneous counterparts such as $Pd(OAc)_2$ and L-Pd(OAc)₂. Since the compound 2 has higher propensity to undergo the selfpolymerization due to its terminal alkoxysilane, L-Pd(OAc)₂ was prepared (Scheme S1 in the SI) through the complexation between $Pd(OAc)_2$ and compound **1**. Owing to their homogeneity in nature, both Pd(OAc)₂ and L-Pd(OAc)₂ showed slightly higher conversion of styrene under given conditions (Table 3, entries 5 and 6). However, Pd(OAc)₂ offered significantly low production yield of acetophenone. Although the production yield of acetophenone in the case of L-Pd(OAc)₂ was found to be better than Pd(OAc)₂, it was still much lower than that of the developed Pd/PMOs. The comparison studies clearly indicate better performance of Pd/PMOs than the homogeneous counterparts in terms of the selectivity and recyclability.

A series of catalytic experiments using the best catalyst, *i.e.* Pd/ PMO-3, were carried out in order to understand the variation from styrene to acetophenone as a function of the reaction time (Fig. 7). The results indicate that the conversion rate increases quite remarkably upon increasing the reaction time, showing the conversion enhancement from 40% for 3 h of reaction to 100% for 10 h of reaction. The highest TOF_A of the catalyst under the given reaction conditions was observed at 5 h, which was recorded as $29.7 h^{-1}$. Apparent decrease of TOF_A upon increasing the reaction time is due to the formations of benzaldehyde and benzoic acid,

Table 3

Catalytic activities of different catalysts in terms of styrene conversion and selectivity of different products.^a

No	Catalyst	Reaction time (h)	n) Conversion of styrene (mol%)	Selectivity of products (mol%)			$TOF_A (h^{-1})^b$
				Acetophenone	Benzaldehyde	Benzoic acid	
1	-	10	3	-	65	35	0
2	Pd/PMO-1	5	51	>99	Trace	-	20.2
3	Pd/PMO-2	5	66	>99	Trace	-	26.1
4	Pd/PMO-3	5	75	>99	Trace	-	29.7
5	$Pd(OAc)_2$	5	82	18	48	34	7.0
6	$L-Pd(OAc)_2$	5	79	73	16	11	28.9

^a Reaction conditions: styrene/H₂O₂ = 1:3 (mole ratio), styrene/catalyst = 200:1 (mole ratio), acetonitrile as solvent at 60 °C.

^b TOF_A: turnover frequency, *i.e.*, moles of desired product (acetophenone) formed per mole of active catalytic center per hour.



Scheme 3. Possible catalytic products from the oxidation of styrene.



Scheme 4. Proposed catalytic mechanism of using Pd/PMO catalysts for selective oxidation of styrene to acetophenone with H₂O₂ as oxidant.

which were also observed in the absence of the catalyst. When the reaction continued up to 12 h, the yield of acetophenone was further decreased to 92%, giving rise to few other byproducts.

It is well-known that catalytic oxidation of styrene using H_2O_2 as oxidant can undergo different pathways to afford various possible oxidized products, where styrene oxide, benzaldehyde, benzoic acid, 1-phenylethane-1,2-diol, and phenylacetaldehyde are primarily via Path 1, as well as acetophenone and 1,3-diphenyl-1-butene are mainly via Path 2 (Scheme 3) [29,42]. Based on the obtained result (Table 3, entry 1), in the absence of any catalyst, styrene undergoes Path 1 to afford benzaldehyde, which is further oxidized to produce benzoic acid. Upon the introduction of Pd/PMO catalysts, styrene adopts Path 2 to give acetophenone. All the three

Pd/PMOs prefer Path 2 over Path 1. As a result, markedly high acetophenone production was able to achieve.

Based upon previously reported work [29,43], we proposed an analogous catalytic mechanism using Pd/PMO catalysts for selective oxidation of styrene to acetophenone with H_2O_2 as oxidant in the absence of copper or indium salts as cocatalyst (Scheme 4). According to the proposed mechanism, immobilized Pd^{2+} forms a palladium hydroperoxidic species by the addition of H_2O_2 (Scheme 4, step 1). This species is responsible for transferring oxygen to the olefin through a pseudocyclic hydroperoxypalladation process of the coordinated olefin, leading to the formations of corresponding ketone and palladium hydroxyl species (Scheme 4, step 3). In the presence of an additional H_2O_2 , this palladium hydroxyl



Fig. 8. Catalytic activities of Pd/PMO-3 in terms of styrene conversion and selectivity of different products as a function of H_2O_2 :styrene ratios. Reaction conditions: styrene/catalyst = 200:1 (mole ratio), 30 mL of acetonitrile as solvent at 60 °C.

species regenerates the palladium hydroperoxidic species, completing the catalytic cycle (Scheme 4, step 4). The fate of the intermediate, palladium hydroxyl species, could be different in the presence of low amount of H_2O_2 , where hydroxypalladation of ole-fin will take place, affording Pd(0) and causing the deactivation of the catalysts (Scheme 4, step 5). Thus, low amount of H_2O_2 always disfavors the regeneration of active Pd²⁺ species.

In order to prove the hypothesized mechanism, another series of catalytic reactions were carried out to realize the variation of the conversion and selectivity as a function of different H₂O₂:styrene (H:S) molar ratios. The obtained results (Fig. 8) indicate that the conversion rate increases quite remarkably when the ratio increases, showing the conversion enhancement from 26% for a ratio of 1:1 to 84% for a ratio of 5:1. A consistent yield of 100% for the acetophenone production was observed when the H:S was up to 3:1. Furthermore, the production yield of acetophenone decreases to 93% and 90% for the H:S of 4:1 and 5:1, respectively. The apparent decrease in the production yield upon increasing the H:S molar ratio is due to the formation of benzaldehyde and benzoic acid through Path 1 (Scheme 3) under the influence of high concentration of oxidant. On the other hand, TOFA follows an increasing trend upon the increase of H:S under given reaction time, mainly due to the increase in the total conversion of styrene to acetophenone (Fig. S15 in the SI), So far, all experiments were carried out by adding H₂O₂ in several portions over a long period of time, preventing its rapid decomposition.

Similar catalytic tests were performed for the H:S ratios of 3:1, 4:1, and 5:1, where H_2O_2 was added in a single portion at the beginning of the reactions (Fig. 8). A significant decrease in the conversion of styrene was observed, which can be attributed to the unwanted decomposition of H_2O_2 . In addition, the production yield of acetophenone also decreased significantly, resulting in much lower TOF_A as compared to the previous cases, where H_2O_2 was added in several portions over a long period of time (Fig. S15 in the SI). The deactivation of catalytic activity can be ascribed to the formation of Pd(0) species on account of rapid decomposition of H_2O_2 to result in incomplete catalytic cycle (Scheme 4, step 5). The formation of metallic Pd(0) nanoparticles was observed from the catalysts used in the reactions with one



Fig. 9. Catalytic recycling experiments of Pd/PMO-3 by maintaining the reaction time of 5 h in each cycle. Reaction conditions: styrene/H₂O₂ = 1:3 (mole ratio) with a slow addition of oxidant, styrene/catalyst = 200:1 (mole ratio), 30 mL of acetonitrile as solvent at 60 °C.



Fig. 10. Catalytic recycling experiments of Pd/PMO-3 by maintaining the reaction time of 10 h in each cycle. Reaction conditions: styrene/H₂O₂ = 1:3 (mole ratio) with a slow addition of oxidant, styrene/catalyst = 200:1 (mole ratio), 30 mL of acetonitrile as solvent at 60 °C.

portion addition of H_2O_2 , whereas similar nanoparticles cannot be observed in the catalysts used in the previous cases with several portion additions of H_2O_2 (Figs. S16D and S16E in the SI). Thus, it can be concluded that prolonged addition of H_2O_2 supplies accessible peroxide during the course of the reaction, inhibiting the catalyst deactivation.

In the catalytic recycling experiments, the reactions were carried out for 5 h and 10 h, respectively, by maintaining a slow addition of H₂O₂ over a period of 3 h with an H:S ratio of 3:1. In the case of 5 h reactions (Fig. 9), Pd/PMO-3 presents a good recyclability toward the acetophenone formation with over 99% of styrene conversion up to 3 cycles. A slight catalytic deactivation was observed in the 4th and 5th catalytic cycles. The ICP analysis of the reaction mixture after the 5th catalytic cycle reveals no metal leaching during the catalysis. Similarly, the ICP analysis of Pd/PMO-3 recovered after the 5th catalytic cycle eliminates the metal leaching from the solid catalyst (Table 2). The hot filtration test was also carried out, and no detectable leaching of Pd was observed by the ICP analysis (See the section 10 in the SI for more details). Moreover, the formation of unwanted Pd(0) nanoparticles was ruled out on the basis of the evidence obtained from the TEM and XPS experiments of the used catalyst (Fig. S16B and S16C in the SI). On the other hand, progressive decreases in the conversion as well as in the production yield of acetophenone were observed when the catalytic recycling experiment of Pd/PMO-3 was carried out for 10 h (Fig. 10). The obvious deactivation of Pd/PMO-3 can be attributed to the progressive formation of Pd(0) nanoparticles, which were observed in the TEM images (Fig. S16F, S16G, and S16H in the SI). The reason is that, when the reaction was carried out for 10 h, the amount of H_2O_2 decreased remarkably, resulting in the formation of Pd(0)nanoparticles.

4. Conclusions

In conclusion, we have successfully synthesized a type of PMOs using β -diketiminate as the bridging unit within the silica network. Highly mesoporous architecture together with the β -diketimine centers enable the PMOs to serve as an ideal scaffold for coordinating with Pd(OAc)₂ for heterogeneous catalysis. The robust incorporation of Pd(OAc)₂ into the PMOs through the formation of β-diketiminato-acetate Pd²⁺ complex facilitates molecular distribution of metal cation and prevents the formation of Pd(0) nanoparticles. The profound influence of H₂O₂ in the catalysis as well as the catalyst regeneration has been explored experimentally. For the purpose of catalytic application, it has been demonstrated that the incorporation of a homogeneous catalyst, $Pd(OAc)_2$, into PMOs not only improves the selective conversion of styrene toward the acetophenone production, but also affords an excellent recyclability of the heterogeneous PMO catalyst, making the catalytic process more benign from environmental and commercial point of view. Thus, the current work presents a heterogeneous green catalyst for direct production of acetophenone from styrene with high catalytic conversion, selectivity, and recyclability.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.07.019.

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