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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 H_2O_2 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 H_2O_2 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, 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 Pd^{2+} 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 $CuCl_2$ 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 CO_2 [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**)

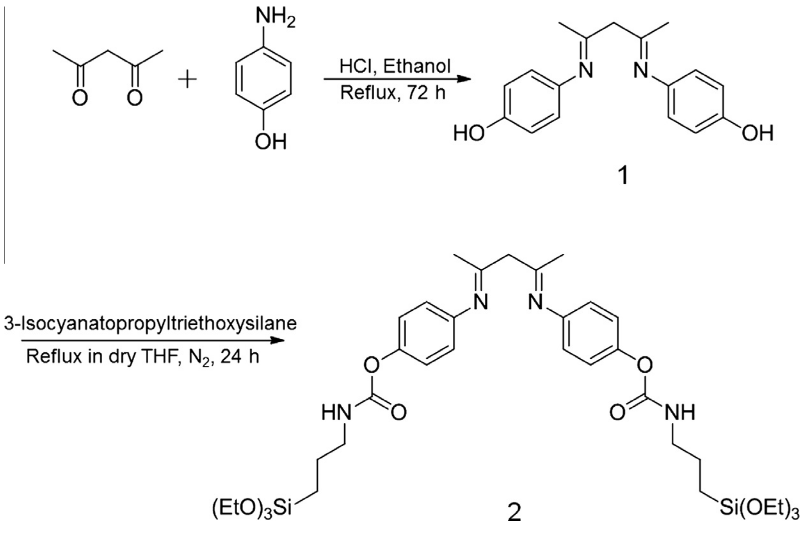
β-Diketimine (**1**) was synthesized according to a reported method with some modifications [12]. In a typical synthesis (Scheme 1), acetylacetone (1.0 g, 10 mmol) and 4-aminophenol (2.2 g, 20 mmol) were dissolved in absolute ethanol (50 mL) in a round bottom flask (100 mL) containing a magnetic stir 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 Na_2CO_3. The solution was extracted with dichloromethane for three times (20 mL each). The organic layer was dried through $MgSO_4$ 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 (CD_3OD, 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); ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ 158.9, 153.4, 142.3, 121.2, 118.6, 40.0, 23.2; IR: ν 3430, 3062, 2852, 1680, 1610, 1594 cm^{-1}; MS: calcd for $C_{17}H_{18}N_2O_2$ $m/z = 282$, 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-triethoxysilylpropylcarbamate) (**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 N_2 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 (CD_3OD, 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); ^{13}C NMR (400 MHz, $CDCl_3$, 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: ν 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: NH_3 (25%): H_2O: 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**.