Molecular Catalysis 433 (2017) 291–300

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

MCAT

Editor's choice paper

Distinctive ligand effects of functionalized magnetic microparticles immobilizing palladium acetate as heterogeneous coordination catalysts for selective oxidation of styrene to acetophenone

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ARTICLE INFO

Article history:
Received 19 January 2017
Received in revised form 15 February 2017
Accepted 18 February 2017

Keywords:
Ligand effect
Heterogeneous coordination catalysts
Selective oxidation
Styrene
Acetophenone

ABSTRACT

A series of functionalized magnetic nanoparticles immobilizing palladium acetate with different ligands, including β-diketimine, Schiff base and (3-aminopropyl)triethoxysilane (APTES), were prepared by a facile surface modification method. These prepared heterogeneous coordination catalysts were characterized by TEM, XRD, FT-IR, VSM, XPS and ICP. Fe_3O_4@SiO_2-β-diketimine was found to be an excellent scaffold for the immobilization of palladium acetate through the complexation between palladium acetate and nitrogen atoms (and oxygen atoms). Among the three catalysts, Fe_3O_4@SiO_2-β-diketimine-Pd(OAc)$_2$ with the highest steric hindrance exhibited extraordinary catalytic property to undergo Wacker type reaction with a high selectivity of 94% toward the formation of acetophenone in liquid phase using H_2O_2 as oxidant. Meanwhile, Fe_3O_4@SiO_2-Schiff base-Pd(OAc)$_2$ and Fe_3O_4@SiO_2-APTES-Pd(OAc)$_2$ afforded 49% and 32% selectivities of acetophenone, which were just a little higher than homogeneous Pd(OAc)$_2$ (15%). Importantly, the proposed reaction mechanism of the styrene selective oxidation reactions by ligand immobilized Pd(OAc)$_2$ catalyst was also inferred according to the distinctive catalytic activities of the three heterogeneous coordination catalysts and reported literatures. It could be concluded that the steric hindrance of the ligand probably played an important role in the selective oxidation of styrene, and big steric hindrance of the ligand probably was beneficial to form acetophenone. Furthermore, Fe_3O_4@SiO_2-β-diketimine-Pd(OAc)$_2$ revealed high efficiency and stability during recycling stages.

1. Introduction

The palladium(II)-catalyzed oxidation of terminal olefins to methyl ketones, known as the Tsuji–Wacker oxidation, is one of the most important reactions that have extensive synthetic applications in laboratories and industries [1–10]. Acetophenones, as significant intermediates for the manufacture of a variety of chemical products such as pesticides, perfumes, pharmaceuticals and resins, can be reasonably obtained by palladium(II)-catalyzed oxidation of styrene [10–16]. Classically, the reaction is conducted with $PdCl_2$ and CuCl as homogeneous catalyst under aerobic atmosphere [2]. However, it suffers from palladium decomposition, chlorinated by-products, copper waste and expensive cost, which has been recognized as significant limitations [17,18]. In addition, the selective oxidation of styrene to acetophenone is often accompanied with other problems, such as difficulties in the product separation, low selectivity, uses of acetic acid and $CuCl_2$ to promote the reoxidation of Pd(0) into highly active Pd(II) resulting in the corrosion hazards of the reactor [15,19].

Many catalytic systems have been developed to solve these major drawbacks for the selective oxidation of styrene to acetophenone, such as avoiding copper(II) salts [19], using various alternative solvent [20–23], using ionic liquids [13,24], and using supported catalysts [20,25,26]. Among the heterogeneous catalytic systems, Zhao et al. have reported an efficient green catalyst for selective oxidation of styrene with H_2O_2 as oxidizing agent [15]. In Zhao's work, periodic mesoporous organosilica supported β-Diketimine was used as a scaffold for immobilization of palladium acetate. As we all know, a variety of organic ligands, such as silane coupling agent containing nitrogen, Salen ligands and Schiff base, also can be used to immobilize palladium acetate to form supported

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http://dx.doi.org/10.1016/j.mcat.2017.02.028
2468-8231/

$Pd(OAc)_2$ catalyst. How will their catalytic activities be compared with β-Diketimine?

On the other hand, since the traditional heterogeneous catalysts are readily dispersed in liquid media by Brownian motion, the separation process of catalysts is still a big challenge. This issue can be solved by using a magnetic material such as Fe_3O_4, so as to be separated by an external magnetic field. Furthermore, the surface of Fe_3O_4 microparticles can be improved by coating chemically modified shells [27–39]. Silica is the most popular inorganic coating material for Fe_3O_4, because it very easily binds to Fe_3O_4 [30–32]. Silica as the coating shell improves the water solubility and biocompatibility of Fe_3O_4. Importantly, the dense silica shell has plenty of Si–OH groups for potential derivatization with various functional units allowing the introduction of catalytic molecules into Fe_3O_4 [35].

Herein, different ligands, including β-diketimine, Schiff base and APTES, were used to functionalize magnetic microparticles and immobilize palladium acetate with a facile surface modification method. The immobilization abilities and stabilities of active sites in the three heterogeneous coordination catalysts were tested with a facile experiment. And the proposed mechanism of the distinctive ligand effects for Wacker reaction was inferred. To our best knowledge, ligand effects on magnetic core-shell material for catalytic reaction have not been reported. Moreover, the recycling performances of these catalysts were also determined.

2. Experimental

2.1. Chemicals

Iron(III) chloride hydrate, sodium acetate, ethylene glycol, trisodium citrate, tetraethyl orthosilicate (TEOS), Palladium(II) acetate, acetylacetone, 4-aminophenol, hydrochloric acid (36%), tetrahydrofuran, diethylenetriamine, salicylaldehyde, triethylamine, acetonitrile, methylbenzene, styrene, ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (3-aminopropyl)triethoxysilane (APTES), 3-isocyanatopropyltriethoxysilane, chloropropyltrimethoxysilane were purchased from Alfa Aesar. All chemicals were of analytical grade and used as received without further purification except tetrahydrofuran and methylbenzene. Deionized water was used throughout the experiments.

2.2. Preparation of catalysts

The preparation process of $Fe_3O_4@SiO_2$-$Pd(OAc)_2$ catalysts were shown in Scheme 1. And the specific process of preparation was listed as follows.

2.2.1. Synthesis of magnetite Fe_3O_4 microparticles

The water dispersible Fe_3O_4 microparticles were prepared according to the reported method previously [40]. Briefly, $FeCl_3 \cdot 6H_2O$ (3.25 g), sodium acetate (NaAc, 6.0 g) and trisodium citrate (1.3 g) were dissolved in ethylene glycol (100 mL). After vigorous stirring, the mixture would become yellow solution, which was then transferred and sealed into a Teflon-lined stainless-steel autoclave (250 mL in capacity). The autoclave was heated at 200 °C for 10 h, and then allowed to cool down to room temperature. The black products were washed with deionized water and ethanol for 3 times, respectively.

2.2.2. Synthesis of magnetic $Fe_3O_4@SiO_2$ composite

The core-shell $Fe_3O_4@SiO_2$ microspheres were prepared through a versatile Stöber sol-gel method as follows [41]. Fe_3O_4 magnetite microparticles (150 mg) was dissolved in the mixture solution of ethanol (280 mL), deionized water (70 mL) and concentrated ammonia solution (5.0 mL, 28 wt%). Afterward, 3.0 mL of TEOS was added dropwise under vigorous stirring in 10 min, and the mixture was allowed to proceed for 10 h at room temperature under continuous mechanical stirring. The resultant core-shell $Fe_3O_4@SiO_2$ microsphere products were separated and collected with a magnet, followed by washing with deionized water and ethanol for 3 times, respectively [42].

2.2.3. Synthesis of $Fe_3O_4@SiO_2$-$Pd(OAc)_2$ catalysts with different ligands

2.2.3.1. $Fe_3O_4@SiO_2$-β-diketimine-$Pd(OAc)_2$. Firstly, β-diketimine was synthesized according to a reported method [15]. In a typical synthesis, acetylacetone (1.0 g, 10 mmol) and 4-aminophenol (2.2 g, 20 mmol) were dissolved in absolute ethanol (50 mL) in around bottom flask (100 mL) containing a magnetic stir bar. HCl (36%, 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 β-diketimine. The ^1H NMR of the resultant β-diketimine was shown in Supporting information (Fig. S1).

Secondly, in a typical synthesis of β-diketimine ligand, synthesized β-diketimine (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 β-diketiminatobis(4,1-phenylene) bis(3-triethoxysilylpropylcarbamate). The ^1H NMR of the resultant product was shown in Supporting information (Fig. S2).

Thirdly, 0.5 g $Fe_3O_4@SiO_2$ microspheres were suspended in 100 ml toluene solution, then, 1.0 g of the prepared β-diketimine ligand was added under dry nitrogen atmosphere. The mixture was refluxed for 24 h and the resulted solid was magnetically separated, washed with ethanol to remove the unreacted residue of silylating reagent. The obtained $Fe_3O_4@SiO_2$-β-diketimine was vacuum dried in vacuum at 60 °C for 12 h.

Finally, an aqueous solution of $Fe_3O_4@SiO_2$-β-diketimine (500 mg) in acetone (50 mL) was ultrasonicated for 1 h to form a uniform suspension. Subsequently, $Pd(OAc)_2$-acetone (20 mg, 20 mL) solution was added to the suspension with vigorous stirring. And then the solution was stirred at room temperature for 24 h. The product was collected from the solution by an external magnet and washed with deionized water and ethanol. The step was repeated several times before drying in vacuum at 60 °C for 12 h.

2.2.3.2. $Fe_3O_4@SiO_2$-Schiff base-$Pd(OAc)_2$. Firstly, the Schiff base ligand (N,N′-bis(3-salicylidenaminopropyl)amine) was prepared by adding one molecular equivalent of diethylenetriamine to two molecular equivalent of salicylaldehyde dissolved in ethanol at room temperature. After stirring for 15 min, the volume of the solution was reduced until only an oil remained [43].

Secondly, 0.5 g $Fe_3O_4@SiO_2$ microspheres were suspended in 100 ml toluene solution, then, 1.0 g of chloropropyltrimethoxysilane was added under dry nitrogen atmosphere. The mixture was refluxed for 24 h and the resulted solid was magnetically separated, washed with ethanol to remove the unreacted residue of silylating