



Coupling MOF-based photocatalysis with Pd catalysis over Pd@MIL-100 (Fe) for efficient N-alkylation of amines with alcohols under visible light



Dengke Wang, Zhaohui Li*

Research Institute of Photocatalysis, State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350002, People's Republic of China

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ABSTRACT

Pd nanoparticles with an average size of 1.7 nm confined inside a MIL-100(Fe) cavity (Pd@MIL-100(Fe)) were prepared via double-solvent impregnation combined with a photoreduction process. Due to efficient coupling of photocatalytic dehydrogenation and Pd-based hydrogenation, the resultant Pd@MIL-100(Fe) showed significantly superior performance in light-induced N-alkylation of amines with alcohols over Pd/MIL-100(Fe), in which larger Pd nanoparticles (6–12 nm) deposited on the external surface of MIL-100(Fe) were prepared via a conventional single-solvent impregnation followed by a similar photoreduction process. Kinetic studies and controlled experiments revealed that the whole N-alkylation reaction is limited by the photocatalytic alcohol-to-aldehyde dehydrogenation reaction. This is the first demonstration of light-induced N-alkylation of amines by alcohols over M/MOFs nanocomposites and also highlights the great potential of using M/MOFs nanocomposites as multifunctional catalysts for light-induced organic syntheses.

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1. Introduction

As important chemicals, N-alkyl amines are important building blocks for the generation of agrochemicals, pharmaceuticals, and bioactive molecules [1,2]. An attractive route for the production of N-alkyl amines is the direct alkylation of amines with alcohols as alkylating agents, since such a reaction has a high atom efficiency and produces water as the only byproduct [3–6]. Until now, a variety of catalysts, mostly Ru- and Ir-based homogeneous catalysts, as well as some noble metal nanoparticle-doped heterogeneous catalysts, have been developed for N-alkylation of amines with alcohols [7–10]. Unfortunately, the catalytic performance of these systems is far from satisfactory. Usually the homogeneous systems suffer from limited reusability and indispensable use of co-catalysts [11,12], while most of the heterogeneous systems are used under harsh conditions, in which overalkylation occurs. In addition, deterioration of the performance of metal-nanoparticle-based heterogeneous systems is unavoidable due to the aggregation of metal nanoparticles [13]. Therefore, the development of stable and highly efficient heterogeneous catalytic systems for N-alkylation reactions under mild conditions, in particular under solar light irradiation, is highly desirable.

It is widely accepted that the N-alkylation of amines with alcohols follows a hydrogen autotransfer mechanism containing three consecutive catalytic steps: dehydrogenation of alcohols to aldehydes, condensation of aldehydes with amines to imines, and hydrogenation of imines to N-alkyl amines [3–6,14–17]. To realize these consecutive steps in one pot, multifunctional catalysts containing different catalytically active sites are required. Recently, TiO₂-supported Pd, Au, and Cu–Mo nanoparticles have been reported to show activity in this one-pot alkylation reaction under UV light irradiation [18–20]. Although the light-induced alkylation of amines with alcohols is quite appealing, since the reaction conditions are mild and the process requires no co-catalysts, these metal/TiO₂ nanocomposites only take effect under UV irradiation and the aggregation of metal nanoparticles during the reactions, which would deteriorate their activity, cannot be avoided. Additionally, the morphology of the metal nanoparticles plays an important role in their catalytic performance. Small nanoparticles are usually more active, since they contain more coordinated unsaturated sites, which are the actual active sites for catalytic reaction [18]. However, size-controllable preparations of metal nanoparticles on the surfaces of semiconductors are usually challenging, since aggregation of these small nanoparticles occurs readily due to their high surface energy.

The employment of the nanopores in porous materials as nanoreactors for direct growth of nanoparticles is a widely adopted

* Corresponding author. Fax: +86 591 83779260.

E-mail address: zhaohuili1969@yahoo.com (Z. Li).

and effective strategy for obtaining nanoparticles with controllable size [21–28]. Metal–organic frameworks (MOFs), a class of hybrid materials with highly ordered uniform nanopores, can provide well-defined microenvironments for controllable growth of nanoparticles [29–44]. Although still in their infancy, metal/MOFs nanocomposites with metal nanoparticles encapsulated inside the cavity have already shown promise in heterogeneous catalysis [45–54]. Photocatalysis is a unique kind of heterogeneous catalysis that involves the use of a light source [55–57]. Recently, MOFs have emerged as a new type of promising photocatalysts due to their tunable light absorption and the ability to organize different functional components in an individual MOF material [58–64]. In addition, the highly crystalline nature of MOFs ensures rapid electron and energy transfer from the photoexcited MOFs to the active sites for a variety of photocatalytic reactions [65–70].

Here, we report the preparation of Pd nanoparticles encapsulated inside the MIL-100(Fe) cavity (Pd@MIL-100(Fe)) via double-solvent impregnation combined with a photoreduction process and its application for light-induced N-alkylation of amines with alcohols. As compared with Pd/MIL-100(Fe), in which larger Pd nanoparticles were deposited on the surface of MIL-100(Fe), Pd@MIL-100(Fe) showed superior catalytic activity and higher stability. For the first time, this work demonstrates the use of the nanopores in MOFs for controllable growth of metal nanoparticles encapsulated inside MOFs as a way to realize a highly efficient and stable alkylation of amines via successful coupling of the MOF-based photocatalysis and metal NPs-based hydrogenation.

2. Experiments

2.1. Preparations

All the reagents were commercially available and used without further purification. MIL-100(Fe) was prepared following the procedures described in the literature with slight modifications [71–74]. Typically, iron(III) nitrate nonahydrate (484 mg, 1.2 mmol) and 1,3,5-benzenetricarboxylic acid (210 mg, 1.0 mmol) were dissolved in deionized water (5 mL). Then the resulting solution was stirred, transferred to a Teflon autoclave liner, and sealed to heat at 180 °C for 12 h. The obtained yellow solid was recovered by filtration and washed several times with deionized water and methanol. The synthesized MIL-100(Fe) was finally dried overnight at 60 °C in an oven.

Pd@MIL-100(Fe) was prepared by a double-solvent impregnation approach combined with a photoreduction process. The double-solvent impregnation approach was first developed by Xu et al. for the preparation of Pt@MIL-101(Cr) and AuNi@MIL-101(Cr) [75,76]. For the impregnation, 100 mg of activated MIL-100(Fe) was suspended in 20 mL of dry *n*-hexane and 0.08 mL of an aqueous solution containing PdCl₂(CH₃CN)₂ (2.46 mg, 1 wt.% Pd) was added dropwise within 15 min under vigorous stirring. After the mixture was stirred for 2 h, the solid was isolated from the supernatant by decanting, washed with ethanol, and dried under vacuum. The as-obtained solid product was then suspended in degassed anhydrous methanol and was irradiated under visible light for 3 h. The resultant sample was filtered, washed with methanol, and dried overnight at 60 °C in an oven.

For comparison, Pd/MIL-100(Fe) was synthesized employing the direct photoreduction method via a conventional single-solvent impregnation process. A quantity of 0.08 mL of an aqueous solution of PdCl₂(CH₃CN)₂ (2.46 mg, 1 wt.% Pd) was added to the degassed anhydrous methanol (5 mL) containing 100 mg of MIL-100(Fe) under N₂. The as-obtained suspension was irradiated under visible light for 3 h. The resultant solid was filtered, washed with methanol, and dried overnight at 60 °C in an oven. Pd/Fe₂O₃

and Pd/TiO₂ were prepared similarly to Pd/MIL-100(Fe) except that UV light (254 nm) was used for the preparation of Pd/TiO₂.

2.2. Characterizations

X-ray diffraction (XRD) patterns were collected on a D8 Advance X-ray diffractometer (Bruker, Germany) with Cu K α radiation. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. Data were recorded at a scanning rate of 0.02° 2 θ s⁻¹ in the 2 θ range of 5–30°. UV–visible diffuse reflectance spectra (UV-DRS) of the powders were obtained with BaSO₄ used as a reflectance standard. BET surface area was determined on an ASAP 2020M apparatus (Micromeritics Instrument Corp., USA). The samples were degassed under vacuum at 150 °C for 10 h and then measured at –196 °C. The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL model JEM 2010 EX instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum 2000 XPS system (PHI, USA). Inductively coupled optical emission spectrometry (ICP-OES) was performed on Optima 8000 (PerkinElmer). Before the ICP-OES experiment, the solid sample was digested in a mixture of HNO₃ and Milli-Q water.

2.3. Catalytic reactions

The N-alkylation reaction was performed in a sealed reaction tube under visible light irradiation. The catalyst (10 mg), amine (0.1 mmol), and alcohol (3 mmol) were suspended in acetonitrile (CH₃CN, 2 mL) and the resultant mixture was degassed and saturated with N₂ to remove any dissolved O₂ before the reaction. The reaction was performed under irradiation by a 300 W Xe lamp equipped with a UV-cut filter to remove all irradiation with wavelengths less than 420 nm and an IR-cut filter to remove all irradiation with wavelengths greater than 800 nm. After the reaction, the reaction mixture was filtered through a porous membrane (20 μ m in diameter) and the products were analyzed by GC-MS and GC-FID (Shimadzu GC-2014) equipped with an HP-5 capillary column.

Photocatalytic dehydrogenation of benzyl alcohol was conducted in a sealed reaction tube containing Pd@MIL-100(Fe) (10 mg), benzyl alcohol (0.1 mmol), and CH₃CN (2 mL).

Hydrogenation of N-benzylideneaniline with H₂ was carried out in a reaction tube containing Pd@MIL-100(Fe) (10 mg), N-benzylideneaniline (0.1 mmol), benzyl alcohol (3 mmol), and CH₃CN (2 mL).

Hydrogenation of N-benzylideneaniline over H₂-pretreated Pd@MIL-100(Fe) was carried out in a Schlenk tube. Pd@MIL-100(Fe) was first activated and treated with H₂ for 1 h at 120 °C in the tube. Then the H₂ was removed, followed by filling the tube with N₂. Finally, CH₃CN solution (2 mL) containing N-benzylideneaniline (0.1 mmol) was added and stirred under room temperature.

The catalytic reaction between aniline and benzaldehyde was carried out in a tube containing Pd@MIL-100(Fe) (10 mg), aniline (0.1 mmol), benzaldehyde (0.5 mmol), and CH₃CN (2 mL).

The deuterium-labeling experiments were conducted using benzyl alcohol and benzyl alcohol- α,α -d₂ as alkylating agent. The kinetic isotope effect (KIE) is defined as k_H/k_D , in which k_H and k_D are the rate constants for the alkylation reactions carried out over benzyl alcohol and benzyl alcohol- α,α -d₂, respectively.

3. Results and discussion

MIL-100(Fe) was chosen as the host matrix to encapsulate Pd nanoparticles due to its good resistance to water and organic

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