



Highly dispersed palladium nanoparticles supported on amino functionalized metal-organic frameworks as an efficient and reusable catalyst for Suzuki cross-coupling reaction



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ABSTRACT

Palladium nanoparticles (Pd NPs) supported on amino functionalized UiO-66-NH₂ (UiO = University of Oslo) metal-organic framework was prepared using a direct anionic exchange method followed by chemical reduction with sodium acetate in methanol. This nano palladium containing catalyst was characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), N₂ adsorption, inductively coupled plasma atomic emission spectroscopy (ICP-AES), field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The Pd/UiO-66-NH₂ catalyst showed excellent activity in Suzuki–Miyaura cross-coupling reaction and reused several times without any appreciable loss of activity even after five consecutive times.

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Introduction

Palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of aryl halides with arylboronic acids have been accredited as one of the most powerful and convenient synthetic tools available to construct unsymmetrical biaryl compound [1]. Homogenous palladium catalysts provide high turnover number and high activity but they often suffer from difficulty of recycling and separation from the products [2]. So it is favorable to develop heterogeneous catalysts for Suzuki reactions to solve such problems [3]. However, palladium nanoparticles as an important kind of heterogeneous catalysts usually undergo aggregation and lose their catalytic activity in the absence of a suitable stabilizer or protecting agent [4]. It is a well-known fact that immobilization of Pd nanoparticles on solid support makes the catalyst effective and recyclable and minimizes the leaching of the particles.

Metal-organic frameworks (MOFs), a new family of organic–inorganic hybrid materials, consist of coordination centers bounded by organic linkers. Due to their tunable cavities, various topologies, porosity and extraordinary surface areas, MOFs have

emerged as promising functional materials for gas sorption or storage [5], drug release [6], luminescence [7], optoelectronics [8,9], chemical sensing [10] and catalysis [11–14].

In recent decades, a number of solid materials, such as polymers [15], carbon structures [16], zeolites [17] and mesoporous silica [18] have been successfully employed as catalyst supports. MOFs can be used as supports for Pd NPs owing to their unique structural features such as well-defined pore structure, narrow micropore distribution and ultimately large surface areas [19]. In fact, the pores of MOFs can prevent migration and aggregation of the metal nanoparticles. Several reviews describe the use of metal-organic frameworks (MOFs) as porous matrices to embed metal nanoparticles (MNPs) [20,21]. A recent review by Moon et al. summarized different methods for preparation of metal NPs within MOF materials [22]. Although there are several methods for loading palladium nanoparticles onto porous MOFs using surface grafting methods and solution infiltration [23–25], because of the easy agglomeration and leaching into solution, developing of an effective and facile method to incorporate Pd NPs on MOFs remains a big challenge [14,19,26,27]. Recently amino functionalized metal-organic frameworks have attracted tremendous attention for this purpose. It seems that the uncoordinated amine groups of these MOFs can stabilize Pd NPs and prevent their agglomeration. Huang et al. reported the preparation of Pd NPs supported on amine-functionalized MIL-53(Al)-NH₂ and MIL-53(Al) and their

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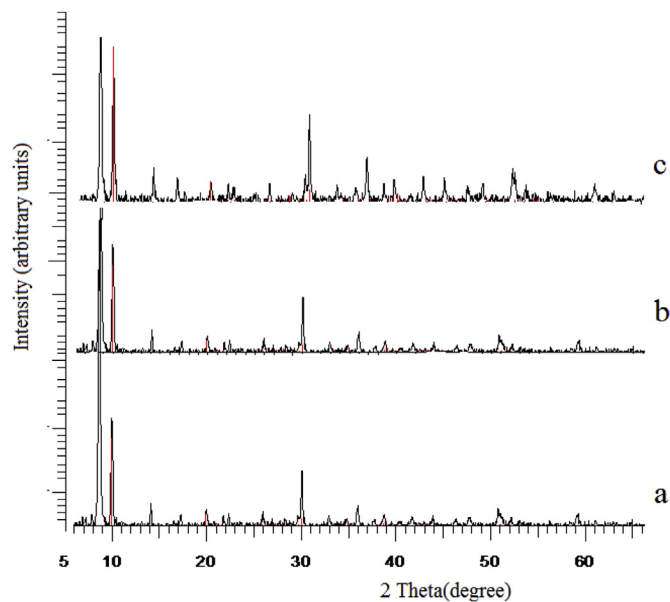


Fig. 1. XRD patterns of UiO-66-NH₂ samples: (a) activated UiO-66-NH₂; (b) fresh Pd/UiO-66-NH₂ and (c) Pd/UiO-66-NH₂ after five catalytic cycles.

application in Suzuki and Heck reactions [28,29]. Yamashita et al. immobilize Pd NPs within the pores of MIL-125 MOF and its amine-functionalized NH₂-MIL-125 by photo-assisted and ion exchange deposition methods and used them for hydrogen production at ambient temperature [30]. They showed that the amine groups in NH₂-MIL-125 increased the H₂-generating activity and acted as a stabilizer of Pd NPs. Xu et al. successfully immobilized bimetallic Au–Pd nanoparticles (NPs) in the MIL-101 MOF and ethylenediamine (ED)-grafted MIL-101 (ED-MIL-101) using a simple liquid impregnation method as a first highly active MOF immobilized metal catalysts for conversion of formic acid to hydrogen [31].

Lillerud et al. synthesized the first example of a zirconium(IV) dicarboxylate MOF named UiO-66 by a conventional solvothermal method [32]. Recently Cohen et al. synthesized and characterized amino functionalized UiO-66-NH₂ and introduced specialized functionalities through a postsynthetic modification (PSM) approach [33]. UiO-66-NH₂, which has uncoordinated amine groups, is based on a 3-D structure of zirconium-oxo clusters [33]. It has been established that the amino group in UiO-66-NH₂ are chemically available, as evidenced by the H/D exchange experiment, so this MOF is very interesting in the field of catalysis [34]. One of the important key points for using of MOFs is their thermal and chemical stability. The UiO-66-NH₂ contains a highly stable secondary building units (SBU), comparable to the parent UiO-66 material, which leads to an

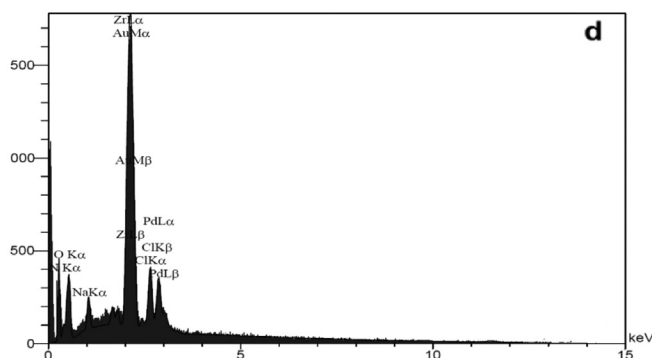
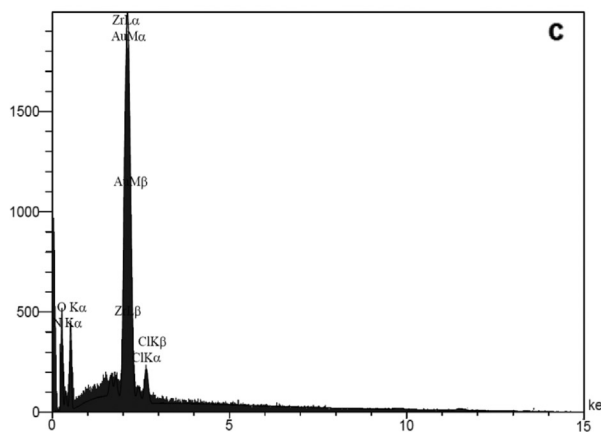
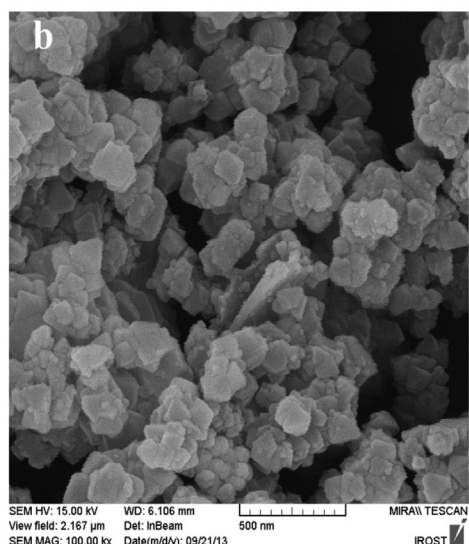
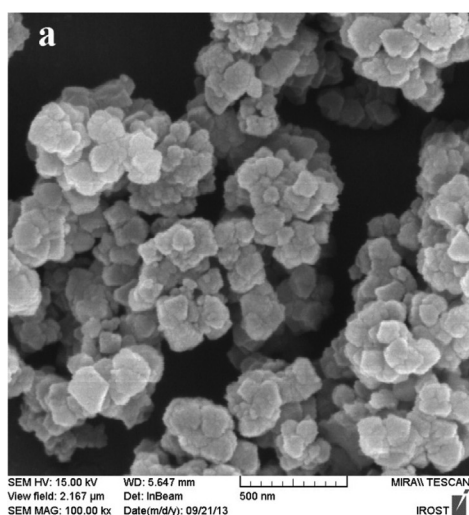


Fig. 2. FE-SEM image of: (a) activated UiO-66-NH₂ and (b) Pd/UiO-66-NH₂. SEM-EDX spectrum of: (c) activated UiO-66-NH₂ and (d) Pd/UiO-66-NH₂.

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