Chemical Engineering Journal 328 (2017) 977–987

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

# Pd nanoparticles encaged within amine-functionalized metal-organic frameworks: Catalytic activity and reaction mechanism in the hydrogenation of 2,3,5-trimethylbenzoquinone

Shuang Zheng, Pengyong Yang, Fumin Zhang *, De-Li Chen *, Weidong Zhu

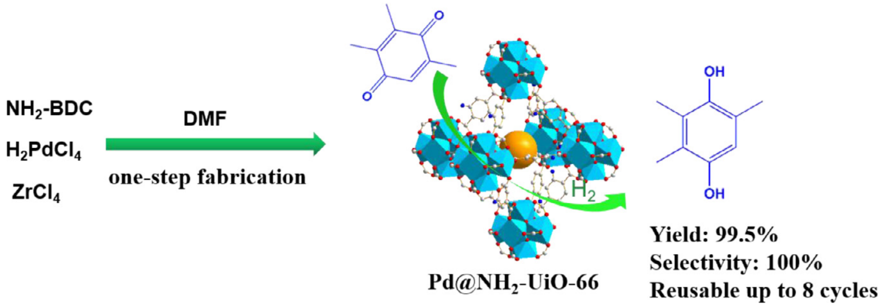
*Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, 321004 Jinhua, People's Republic of China*

## HIGHLIGHTS

- Pd@$NH_2$-UiO-66 synthesized by a facile one-pot strategy under dynamic condition.
- Pd@$NH_2$-UiO-66 shows high catalytic properties in hydrogenation of TMBQ to TMHQ.
- Pd@$NH_2$-UiO-66 is a promising candidate for catalytic hydrogenation reactions.
- Cooperation between Pd nanoparticle and $NH_2$-UiO-66 leads to the high activity.

## GRAPHICAL ABSTRACT

The Pd@$NH_2$-UiO-66 prepared by the one step strategy exhibits excellent catalytic properties in the hydrogenation of TMBQ to TMHQ under mild reaction conditions.



## ARTICLE INFO

*Article history:*
Received 29 March 2017
Received in revised form 7 July 2017
Accepted 15 July 2017
Available online 16 July 2017

*Keywords:*
Metal-organic frameworks
$NH_2$-UiO-66
2,3,5-Trimethylbenzoquinone
Catalytic hydrogenation
Reaction mechanism
Density functional theory

## ABSTRACT

Pd nanoparticles encaged within an amine-functionalized metal-organic framework (MOF), Pd@$NH_2$-UiO-66, was successfully prepared via one pot direct construction of the MOF framework, cooperative *in situ* metal precursor incorporation followed by on-site moderate reduction process. Because of its abundant of nanocages accessible through small pore windows, as well as excellent coordination capability of metal ions sites from the amine groups within the $NH_2$-UiO-66 matrix, the Pd nanoparticles were homogeneously confined within its cavities. Intriguingly, the prepared Pd@$NH_2$-UiO-66 exhibits a high catalytic activity and exclusive selectivity in the liquid-phase hydrogenation of 2,3,5-trimethylbenzoquinone (TMBQ) to 2,3,5-trimethylhydroquinone (TMHQ), a key vitamin-E intermediate in a short period under relatively mild reaction conditions. Additionally, this catalyst was recycled up to 8 times without significant loss in both activity and selectivity. Furthermore, reaction mechanism was investigated using dispersion corrected density functional theory calculations, suggesting that the superior performance of Pd@$NH_2$-UiO-66 could be ascribed to the cooperation between the Pd nanoparticle and the amine-functionalized UiO-66. This MOF-based composite shows great potential as heterogeneous catalyst for the catalytic hydrogenation reactions due to its high stability, excellent catalytic properties, and simple preparation.

---

* Corresponding authors.
*E-mail addresses:* zhangfumin@zjnu.edu.cn (F. Zhang), chendl@zjnu.cn (D.-L. Chen).

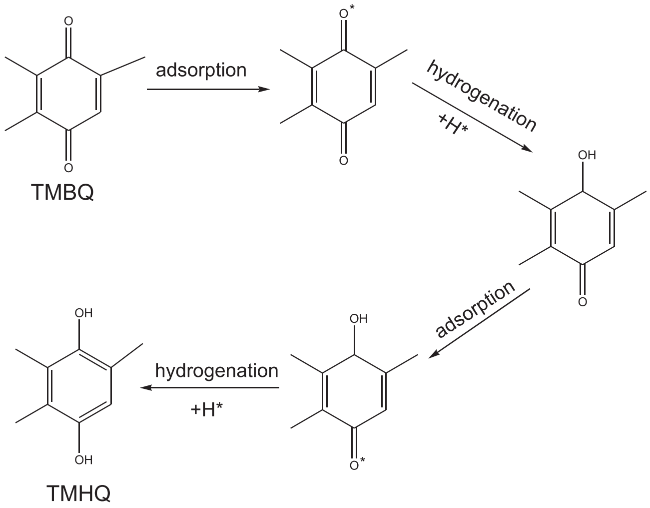
http://dx.doi.org/10.1016/j.cej.2017.07.099
1385-8947/

## 1. Introduction

Noble metals, such as Pd, Pt, and Ru, supported on a variety of supports were often recognized as effective heterogeneous catalysts for catalytic hydrogenation reactions because of their unique catalytic properties [1–4]. The electronic and textural properties of the support usually exert significant influence on the catalytic performance in terms of the dispersion and state of noble metals nanoparticles, the adsorption and diffusion of substrates and products, and so on [5–8]. In general, the prerequisite for an ideal support is that it could well encapsulate/disperse the metal nanoparticles, facilitate the adsorption of reactants, and accelerate the diffusion of products. By tuning the host-guest interaction between the metal nanoparticles and the supports, it is plausible to obtain an efficient synergetic catalysis over the potential supported catalysts [9,10]. Therefore, a numerous of porous materials including activated carbon, aluminum oxide, silica gel, zeolite, mesoporous silica, carbon nanotube, and graphene have been investigated as noble metals supports during the past few decades [10–18]. However, the noble metals nanoparticles introduced onto the above mentioned porous materials usually suffer from serious leaching or aggregation problem in the catalytic reactions, which inevitably causes negative effect on the catalytic activity and recyclability.

Metal-organic frameworks (MOFs), emerging as a type of crystalline porous materials, are self-assembled by the coordination of metal cations/clusters with organic linkers [19–21]. Due to their large specific surface areas, well-defined pore sizes, and controllable internal microenvironments, MOFs render enormous possibility in the realm of heterogeneous catalysis [22–26]. The introduction of noble metal nanoparticles into the cavities of MOFs have attracted great interests, as the controllable growth as well as the uniform distribution of metal nanoparticles within the MOFs can be well engineered by the rational construct of the frameworks with required pore sizes [27–30]. On the other hand, the three-dimensional interconnected MOF pores are easily accessible for both substrate and product, which is essential from the enhancing mass-transfer point of view. Briefly, there are two ways for the construction of nanoparticle-MOF composites including encapsulating preformed nanoparticles in MOFs or using MOFs as template to generate nanoparticles in their cavities [31–35]. In the former it is difficult to control the spatial distribution of preformed nanoparticles confined in the MOFs, while in the latter there are many inherent shortcomings such as the aggregation of nanoparticles on the external surface of the MOFs, the poor control of nanoparticles size, and the potential degradation of the MOF frameworks during the post-reduction treatment under harsh conditions.

Recently, Li and coworkers developed a one-step method under static conditions to incorporate Pd nanoparticles into the MOF cavities by using *N,N′*-dimethylformamide (DMF) as both a reductant for Pd metal ions and a solvent for the formation of MOF [36,37]. However, probably owing to the inherent slow mass transfer rate under static conditions, a small portion of the Pd nanoparticles were not encapsulated within the UiO-67, thus leading to uneven and uncontrollable distribution of Pd nanoparticles [36]. In order to conquer this problem, in this work, we developed a one-pot strategy for the preparation of Pd nanoparticles confined in MOFs under dynamic condition (agitation). The amine-functionalized MOF, $NH_2$-UiO-66, was chosen as it has high thermal and chemical stability, abundant cages interconnected by the three-dimensional channel, and excellent coordination capability for metal ions sites from the amine groups within the frameworks [38–43]. Notably, mass transfer would be significantly intensified under agitation conditions, therefore, the assembly of $NH_2$-UiO-66 and the *in-situ* reduction of the encapsulated Pd precursor by DMF could be realized simultaneously, leading to the homogeneous distribution of Pd nanoparticles inside the nanopores of the $NH_2$-UiO-66. In the following, we will investigate the high catalytic activity and exclusive selectivity of the prepared Pd@$NH_2$-UiO-66 in the liquid-phase hydrogenation of 2,3,5-trimethylbenzoquinone (TMBQ) to 2,3,5-trimethylhydroquinone (TMHQ), a key vitamin-E intermediate [44,45], by experiments and density functional theory calculations [46,47]. Two step reaction pathways are proposed for the hydrogenation of TMBQ in Scheme 1, which will be computed and discussed in detail.



**Scheme 1.** The proposed reaction pathways for the hydrogenation of TMBQ to TMHQ using $Pd_{28}$@$NH_2$-UiO-66 as the catalyst.

## 2. Experimental section

### 2.1. Chemicals

All chemicals were from commercial and used without further purification: zirconium (IV) chloride ($ZrCl_4$, Aladdin Industrial Inc., 98%), terephthalic acid (BDC, TCI,>99%), 2-aminoterephthalic acid ($NH_2$-BDC, TCI,>98%), hydrochloric acid (HCl, Sinopharm Chemical Reagent Co., Ltd., 37 wt%), $PdCl_2$ (Aladdin Industrial Inc., 59%-60%), Pd/C (Aladdin Industrial Inc., 5.0 wt%), DMF (Sinopharm Chemical Reagent Co., Ltd., $\geq$99.5%), methanol (Sinopharm Chemical Reagent Co., Ltd., $\geq$99.5%), *i*-propanol (Sinopharm Chemical Reagent Co., Ltd., $\geq$99.7%), acetone (Sinopharm Chemical Reagent Co., Ltd., $\geq$99.5%), dioxane (Aladdin Industrial Inc., 99%), ethanol (Sinopharm Chemical Reagent Co., Ltd., $\geq$99.7%), ethyl acetate (Sinopharm Chemical Reagent Co., Ltd., $\geq$99.5%), toluene (Sinopharm Chemical Reagent Co., Ltd., $\geq$99.5%), cyclohexane (Sinopharm Chemical Reagent Co., Ltd.,$\geq$99.5%), Sulfuric acid ($H_2SO_4$, Sinopharm Chemical Reagent Co., Ltd., 98%), Hydrogen peroxide solution ($H_2O_2$, Aladdin Industrial Inc., 30%), 2,3,5-trimethylhydroquinone (TMHQ, Aladdin Industrial Inc., 98%), 2,3,5-trimethylbenzoquinone (TMBQ, Zhejiang Rainful Chemical Co., Ltd., >99%), and $H_2$ (Shanghai Pujiang Special Gas Co., Ltd, 99.999%). Deionized water with a resistance >18.2 MΩ was obtained from a Millipore Milli-Q ultrapure water purification system

### 2.2. Preparation of Pd@$NH_2$-UiO-66 catalyst

The Pd@$NH_2$-UiO-66 catalyst was prepared by a facile one-pot strategy under dynamic condition without adding any external reducing agent. Typically, $ZrCl_4$ (0.12 g, 0.515 mmol), $NH_2$-BDC (0.093 g, 0.515 mmol), deionized water (0.15 mL) and concentrated