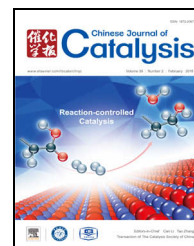


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## Article

# Highly selective hydrogenation of furfural to tetrahydrofurfuryl alcohol over MIL-101(Cr)-NH<sub>2</sub> supported Pd catalyst at low temperature

Dongdong Yin <sup>a,†</sup>, Hangxing Ren <sup>b,†</sup>, Chuang Li <sup>a</sup>, Jinxuan Liu <sup>c,#</sup>, Changhai Liang <sup>a,\*</sup><sup>a</sup> Laboratory of Advanced Materials and Catalytic Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China<sup>b</sup> Purification Equipment Research Institute of CSIC, Handan 056027, Hebei, China<sup>c</sup> State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, Dalian University of Technology, Dalian 116024, Liaoning, China

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## ABSTRACT

An efficient heterogeneous catalyst, Pd@MIL-101(Cr)-NH<sub>2</sub>, is prepared through a direct pathway of anionic exchange followed by hydrogen reduction with amino-containing MIL-101 as the host matrix. The composite is thermally stable up to 350 °C and the Pd nanoparticles uniformly disperse on the metal organic framework (MOF) support, which are attributed to the presence of the amino groups in the frameworks of MIL-101(Cr)-NH<sub>2</sub>. The selective hydrogenation of biomass-based furfural to tetrahydrofurfuryl alcohol is investigated by using this multifunctional catalyst Pd@MIL-101(Cr)-NH<sub>2</sub> in water media. A complete hydrogenation of furfural is achieved at a low temperature of 40 °C with the selectivity of tetrahydrofurfuryl alcohol close to 100%. The amine-functionalized MOF improves the hydrogen bonding interactions between the intermediate furfuryl alcohol and the support, which is conducive for the further hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol in good coordination with the metal sites.

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## 1. Introduction

Recently, research efforts have been devoted to the production of biofuels and biomass-derived chemicals from nonedible lignocellulosic biomass owing to the increasing awareness of energy exhaustion and environmental concerns [1,2]. Furfural (FUR), which is mainly produced from the acidic hydrolysis of hemicellulose and accounts for 25%–35% of the lignocellulosic biomass, has been selected as one of the top 30 biomass-derived platform chemicals and employed as the feed-

stock for the sustainable production of biofuels and value-added chemicals [3–6]. The catalytic hydrogenation of furfural has been extensively investigated, which can be transformed to furfural alcohol (FA) and tetrahydrofurfuryl alcohol (THFA) [7–10]. Hydrogenolysis may also occur during the hydrogenation process which can produce 2-methylfuran, 2-methyltetrahydrofuran, cyclopentanone, cyclopentanol and polyols, such as 1,5-pentanediol and 1,2-pentanediol [11–14].

THFA is widely used as green solvent, for the synthesis of special chemicals, such as dihydropyran, and has also been

\* Corresponding author. Tel/Fax: +86-411-84986353; E-mail: [changhai@dlut.edu.cn](mailto:changhai@dlut.edu.cn)# Corresponding author. Tel: +86-411-84986487; Fax: +86-411-84986245; E-mail: [jinxuan.liu@dlut.edu.cn](mailto:jinxuan.liu@dlut.edu.cn)

† These authors contribute equally to this work.

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proposed for use as a biofuel or as a fuel additive because of its similar properties to kerosene [4,15]. THFA is usually produced by the hydrogenation of FA derived from FUR, and it can be obtained by the direct hydrogenation of furfural in the presence of noble or non-noble metals [16–19]. The production of THFA from furfural has been investigated extensively. Biradar et al. [9] reported an effective complete hydrogenation of furfural using a 3% Pd/MFI catalyst and achieved the highest conversion and THFA selectivity in the range of 93%–100% and 67%–95%, respectively, under optimized conditions of 220 °C and 3.5 MPa. Nakagawa et al. [18] prepared a Ni/SiO<sub>2</sub> catalyst with Ni particle size <4 nm and achieved a maximum THFA yield of 94% for the gas-phase hydrogenation of furfural. They found that the conversion of FA intermediate to THFA was strongly structure sensitive and the turnover frequency (TOF) decreased with increasing metal particle size. The same group also obtained a 94% yield of THFA catalyzed by a large amount of Pd–Ir/SiO<sub>2</sub> (Pd/Ir = 1) bimetallic catalysts in the liquid-phase process and suggested that a high hydrogen pressure (8 MPa) and low reaction temperature (2 °C) were useful to suppress side reactions [20]. However, harsh conditions, such as high hydrogen pressure and high reaction temperature, are usually required for the conversion of FUR to THFA. The design of novel and environmentally-friendly catalysts that can achieve a high THFA selectivity under mild conditions in a green process is of great importance.

Metal organic frameworks (MOFs), which have emerged as a new class of porous materials with diverse properties such as high surface area, permanent porosity and easy functionalization by post-synthetic modification or direct synthesis, have been widely studied and applied in catalysis, in particular, biomass catalysis [21–24]. For example, Zeolitic imidazolate frameworks (ZIFs) were used for the transformation of sugars to lactic acid derivatives with a high conversion and yield [25]. A MOF-based polyoxometalate [Cu-BTC][HPM] showed good catalytic activity in the conversion of 5-hydroxymethylfurfural (5-HMF) [26]. The metal nanoparticles supported on Zr-MOFs were proven to be highly efficient catalysts for biomass refining [27,28]. MIL-101, one of the most stable MOF structures, possesses a high surface area, large porosity, numerous coordinatively unsaturated metal sites and can be subjected to diverse functionalization or guest species encapsulation, and it has been widely used for biomass catalysis [29–32]. The sulfonic-acid-functionalized MIL-101(Cr) [MIL-101(Cr)-SO<sub>3</sub>H] was investigated as a solid acid for the catalytic conversion of glucose to 5-HMF [33]. Noble metal nanoparticles, such as those containing Pd or Ru, incorporated within MIL-101 or organic-functionalized (–SO<sub>3</sub>H, –NH<sub>2</sub>) MIL-101 exhibited a high activity and selectivity in the hydrodeoxygenation or selective hydrogenation of biomass compounds [31,34,35]. It has been demonstrated that the presence of free amine groups in the MOF plays a key role on the formation of uniform, well-dispersed and leaching resistant metal nanoparticles within the MOF host. In addition, the nitrogen-containing support may have an effect on the selectivity towards the target products in hydrogenation reactions [36,37].

Herein, we reported the direct synthesis of

amine-functionalized MIL-101(Cr) [MIL-101(Cr)-NH<sub>2</sub>], which exhibits excellent stability to moisture and acid compared with Fe-, Al- and V-MIL-101. The palladium nanoparticles were loaded into the MOF matrix through a direct anionic exchange approach followed by hydrogen reduction [38,39]. The resulting Pd@MIL-101(Cr)-NH<sub>2</sub> was found to be an efficient multifunctional catalyst for the aqueous selective hydrogenation of FUR to THFA with a selectivity of nearly 100% under mild conditions.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Preparation of MIL-101(Cr)-NH<sub>2</sub>

Amine-functionalized MIL-101(Cr) was hydrothermally synthesized by the direct reaction of Cr(III) and 2-aminoterephthalic acid with assistance from hydroxide based on the previous literature with a slight modification [38]. To be specific, 2-aminoterephthalic acid (0.18 g, 1 mmol) and sodium hydroxide (0.1 g, 2.5 mmol) were dissolved in de-ionized water (7.5 mL) by ultrasonication, where the OH<sup>–</sup> ions could promote the dissolution of organic acid. Then, chromic nitrate hydrate (0.4 g, 1 mmol) was dispersed into the former clear aqueous solution. After ultrasonication for 5 min, the suspension was transferred to a Teflon-lined autoclave and heated at 150 °C for 18 h in a convection oven. After cooling to room temperature naturally, the resulting green precipitate was collected by centrifugation and washed sequentially with de-ionized water, DMF and ethanol several times to remove the excess reagents. The sample was then soaked in hot ethanol with continued heating and stirring at 100 °C for 24 h for further purification, after which the product was dried at 100 °C under vacuum for 12 h.

#### 2.1.2. Preparation of Pd@MIL-101(Cr)-NH<sub>2</sub>

Pd nanoparticles were successfully immobilized on MIL-101(Cr)-NH<sub>2</sub> by a direct anionic exchange and subsequent H<sub>2</sub> reduction. Taking the synthesis of 3.0 wt% Pd@MIL-101(Cr)-NH<sub>2</sub> as an example, activated MIL-101(Cr)-NH<sub>2</sub> (0.5 g) was first dispersed in deionized water (30 mL) by ultrasonication and treated with a suitable amount of diluted HCl to adjust the pH to approximately 4. Then a solution of H<sub>2</sub>PdCl<sub>4</sub> (containing ca. 3.0 wt% of Pd) was added dropwise to the above slurry under vigorous stirring, and the mixture was further stirred for another 24 h. The solid was separated by centrifugation, repeatedly washed with deionized water, followed by drying at 100 °C under vacuum for 12 h. The resulting [MIL-101(Cr)-NH<sub>3</sub><sup>+</sup>]<sub>2</sub>[PdCl<sub>4</sub>]<sub>2</sub><sup>–</sup> sample was reduced in a H<sub>2</sub>/Ar (H<sub>2</sub>/Ar = 20/40 mL min<sup>–1</sup>) flow at 200 °C for 4 h to yield Pd@MIL-101(Cr)-NH<sub>2</sub>. The synthetic procedure is shown in Fig. S1.

#### 2.1.3. Preparation of Pd@MIL-101(Cr)

MIL-101(Cr) was synthesized according to our previous report [40], then an impregnation procedure similar to the above-described was adopted for the incorporation of Pd

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