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Selective hydrogenation of biomass-derived 5-hydroxymethylfurfural using palladium catalyst supported on mesoporous graphitic carbon nitride[☆]

Jiayi Chen^{a,1}, Yao Ge^{a,b,1}, Yuanyuan Guo^a, Jinzhu Chen^{a,c,*}

^aGuangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, Guangdong, China

^bCollege of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, Xinjiang, China

^cCollege of Chemistry and Materials Science, Jinan University, Guangzhou 510632, Guangdong, China

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ABSTRACT

Selective hydrogenation of biomass-derived 5-hydroxymethylfurfural (HMF) to 2,5-dihydroxymethyl-tetrahydrofuran (DHMTFH) with 96% selectivity and a complete HMF conversion is obtained over palladium catalyst supported on mesoporous graphitic carbon nitride (Pd/mpg-C₃N₄) under pressured hydrogen atmosphere in aqueous media. The excellent catalytic performance of Pd/mpg-C₃N₄ is attributed to hydrogen bonding-related competitive interactions between reactant HMF and “intermediate” 2,5-dihydroxymethylfuran (DHMF) with the support mpg-C₃N₄, which leads to a deep hydrogenation of DHMF to DHMTFH.

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1. Introduction

The production of liquid fuels and organic chemicals from plentiful and renewable biomass is a matter of growing interest to reduce dependence on fossil fuel sources [1–4]. Biomass is one of the most abundant carbon-containing renewable resources on earth for the production of chemicals and fuels [5,6]. A recent review critically discussed nano-scale metal-catalysts for valorization of biomass-related cellulose, chitin, lignin and lipids [7]. The platform molecule 5-hydroxymethylfurfural (HMF), a typical representative of the furan family, is viewed as one of the key precursors for the production of chemicals and liquid transportation fuels [8–10]. It can be converted into 2,5-dihydroxymethylfuran (DHMF) and 2,5-dihydroxymethyl-tetrahydrofuran (DHMTFH) with further hydrogenation (Fig. 1) [11,12]. Typically, DHMTFH has been used as a high value added chemical with important applications as a solvent as well as polymer monomer [13,14]. In addition,

DHMTFH can be converted to 1,6-hexanediol which is an important monomer for special applications [11,15–20].

The reaction of HMF to DHMTFH has been studied extensively over various metal catalysts. Previously, Nakagawa and Tomishige investigated selective reduction HMF into DHMTFH by using Ni–Pd bimetallic catalysts [11]. Dumesic and co-workers developed monophasic and biphasic reactor systems for selective transformation of HMF into DHMTFH over ruthenium, palladium, and platinum catalysts [12]. Xu and co-workers achieved the conversion of fructose to DHMTFH by a combination of fructose dehydration and HMF hydrogenation [21]. Very recently, the conversion of HMF to DHMTFH was also investigated over palladium immobilized on metal-organic frameworks [22].

Recently, selective hydrogenations of phenol [23–26], nitrophenol [29], quinolone [30], nitroarenes [31], phenylacetylene [32], benzoic acid [33], styrene [34], and 2-methylfuran [34] were reported by using mesoporous graphitic carbon nitride (mpg-C₃N₄) supported transition metal nanoparticles owing to the unique properties of mpg-C₃N₄ such as a large surface area and accessible crystalline pore walls. Recently, Yan and co-workers reported mesoporous, nitrogen-containing carbon materials from chitin carbonization for heavy-metal (Cr^{VI}, Hg^{II}, Pd^{II}) removal and styrene epoxidation [35]. In addition, the presence of electron-rich nitrogen atoms in the supports can enhance π -binding ability, improve basicity and hydrophilicity, and modify interactions between metal sites, reactant, intermediate, product, and support [23–34,36,37].

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* Corresponding author at: College of Chemistry and Materials Science, Jinan University, Guangzhou 510632, Guangdong, China.

E-mail address: chenjz@jnu.edu.cn (J. Chen).

¹ These authors contributed equally to this work.

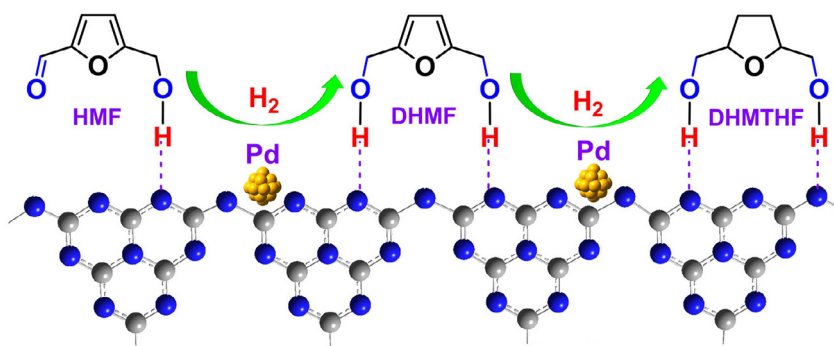


Fig. 1. Molecular interactions in the hydrogenation of HMF over Pd/mpg-C₃N₄.

43 In this research, mpg-C₃N₄ supported palladium (Pd/mpg-C₃N₄)
 44 was investigated as bifunctional catalyst for selective hydrogenation of HMF to DHMTHF under pressured hydrogen atmosphere
 45 yielding DHMTHF selectivity of 96% with a complete HMF conversion (Fig. 1). Our results further indicated that the observed excellent
 46 catalytic performance of Pd/mpg-C₃N₄ is presumably related to hydrogen bonding-related competitive interactions between reactant
 47 HMF and “intermediate” DHMF with the support mpg-C₃N₄, which leads to a deeper DHMF hydrogenation to DHMTHF (Fig. 1).
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52 2. Experimental

53 2.1. Catalyst preparation

54 mpg-C₃N₄: mpg-C₃N₄ was prepared according to the literature
 55 method [37].

56 Pd/mpg-C₃N₄: K₂PdCl₄ (63 mg) in H₂O (40 mL) was treated with
 57 activated mpg-C₃N₄ (500 mg) and the mixture was stirred for 8 h
 58 at 80 °C. Then NaBH₄ (40 mg) solution was added to this suspension
 59 at 0 °C and stirred for 4 h to synthesize Pd/mpg-C₃N₄. Finally,
 60 Pd/mpg-C₃N₄ (Pd 4.1 wt% based on ICP-AES) was separated by filtration,
 61 washed with distilled water and dried at 100 °C overnight
 62 under vacuum.

63 2.2. Characterization of catalyst

64 The Brunauer–Emmett–Teller (BET) surface area measurements
 65 were performed with N₂ adsorption–desorption isotherms at 77 K
 66 (SI-MP-10/PoreMaster 33, Quantachrome), after degassed under
 67 vacuum at 423 K for 12 h. The specific BET surface areas were
 68 evaluated using the method in the p/p_0 range from 0.05 to 0.3.
 69 X-ray diffraction (XRD) patterns were obtained with PANalytical
 70 X’pert Pro multipurpose diffractometer at 40 kV and 40 mA, using
 71 Ni-filtered Cu-K α radiation ($\lambda=0.15418$ nm). High-resolution transmission
 72 electron microscopy (HRTEM) was recorded using a JEM-
 73 2100HR instrument. Samples for HRTEM analysis were prepared by
 74 placing a drop of the suspension sample in ethanol onto carbon-coated
 75 Cu grids, followed by evaporating the solvent. X-ray photoelectron
 76 spectroscopy (XPS) data was obtained with Kratos Axis Ultra
 77 (DLD) photoelectron spectrometer operated at 15 kV and 5 mA
 78 at a pressure of about 5×10^{-9} torr using Al K α as the exciting
 79 source. The binding energies were referenced to the C 1s photo-
 80 electron peak (284.6 eV). Inductively coupled plasma–optical emission
 81 spectroscopy (ICP–OES) analysis was performed with Perkin-
 82 Elmer Optima 8000 instrument.

83 2.3. Selective hydrogenation of HMF to DHMTHF

84 The hydrogenation of HMF under H₂ was conducted in a 60 mL
 85 stainless steel autoclave reactor. HMF (63 mg, 0.5 mmol), Pd/mpg-
 86 C₃N₄ (30 mg, Pd 4.1 wt%) and water (3 mL) were introduced into

the reactor, which was sealed, purged with H₂ three times, and
 pressurized with H₂ (1.0 MPa) at room temperature, and then
 heated to the desired reaction temperature. The reactor was main-
 tained at the desired temperature for 4 h. After the reaction, the reactor
 was cooled to room temperature. Products were separated by
 filtration and water-soluble products were analyzed by HPLC and
 liquid chromatography–mass spectrometer (LC-MS).

2.4. Reusability of the catalyst

After reaction, the catalyst Pd/mpg-C₃N₄ was separated from
 the reaction mixture, and washed with de-ionized water and
 ethanol, dried at 60 °C over night in a vacuum oven. Then, the re-
 covered catalyst was used for the next cycle under the same con-
 ditions.

2.5. Analysis of product

HMF and the hydrogenation products were determined by HPLC
 (Shimadzu LC-20AT) equipped with UV and refractive index (RI) de-
 tectors. The analysis was conducted with a Shodex Sugar SH-1011
 column (300 \times 8 mm) using HPLC grade H₂SO₄ (0.005 M) water so-
 lution as the eluent and a flow rate of 0.5 mL/min at a column
 temperature of 50 °C. The conversion of HMF was determined by
 a UV detector (284 nm); whereas, the concentrations of products
 such as DHMF, DHMTHF and hexanetriol (HT) were monitored by
 an RI indicator.

3. Results and discussion

3.1. Catalyst characterization

As shown from N₂ adsorption/desorption isotherm (Fig. 2),
 the Brunauer–Emmett–Teller (BET) surface area of mpg-C₃N₄ and
 Pd/mpg-C₃N₄ are 145 m²/g and 119 m²/g, respectively. Moreover,
 the BET surface area of Pd/mpg-C₃N₄ decreases from 119 m²/g for
 the fresh one to 98 m²/g for the recovered one after five-time re-
 cycling, indicating the adsorption of humins formed on the surface
 of Pd/mpg-C₃N₄ through the reaction [12].

X-ray powder diffraction (XRD) patterns of mpg-C₃N₄ and
 Pd/mpg-C₃N₄ are compared in Fig. 3. For mpg-C₃N₄, the peak at
 27.4° was a characteristic peak (002) corresponding to the stacking
 of conjugated inter-layers; whereas, the peak at 13.1° was in-
 dexed as (100) showing in-plane ordering of tri-s-triazine units
 (JCPDS 87-1526) [38–40]. Notably, the diffraction peaks of palla-
 dium species in Pd/mpg-C₃N₄ are unobserved (Fig. 3), which is
 presumably due to the small nanoparticles size and high disper-
 sion of noble nanoparticles on the support surface. In addition, the
 XRD patterns of the recovered Pd/mpg-C₃N₄ are almost the same
 as those of fresh one, indicating no apparent loss of crystallinity
 for the recovered catalyst (Fig. 3).

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