



# Room temperature hydrogenation of furfuryl alcohol by Pd/titanate nanotube



Qingqing Yuan, Feiyang Ye, Teng Xue, Yejun Guan\*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, North Zhongshan Road 3663, Shanghai 200062, China

## ARTICLE INFO

### Article history:

Received 11 June 2015

Received in revised form 4 September 2015

Accepted 23 September 2015

Available online 28 September 2015

### Keywords:

Palladium

Furfuryl alcohol

Hydrogenation

Tetrahydrofurfuryl alcohol

Titanate nanotube

## ABSTRACT

The liquid phase hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol at room temperature under 1 atm hydrogen was succeeded on a TiO<sub>2</sub> nanotube (TNT) supported palladium catalyst. The palladium nanoparticles in size of 2–8 nm were loaded by the deposition-reduction method with NaBH<sub>4</sub> as reducing reagent. The Pd/TNT catalyst showed high dispersion as revealed by CO chemisorption and improved catalytic performance in terms of both furfuryl alcohol conversion and tetrahydrofurfuryl alcohol selectivity, probably attributed to the unique electronic interaction between Pd metals and TNT surface containing sodium cations. Among the catalysts investigated, 5.8 wt.% Pd/TNT showed the best performance, with 98% conversion and 98% selectivity to tetrahydrofurfuryl alcohol in ethanol.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Synthesis of tetrahydrofurfuryl alcohol (THFA) from either furfural (FAL) or furfuryl alcohol (FA) is of great industrial interests because THFA is an environmentally benign and biodegradable furanic chemical with low toxicity. It has been broadly used as both intermediate and green solvent in agricultural and industrial applications [1,2]. Recently, THFA has also been proposed to be a promising substrate for the preparation of diols [3,4]. Conventionally THFA is produced by a two-step catalytic hydrogenation of FAL via FA as intermediate over Cu–Cr, Ni or noble metal catalysts [5,6]. The second step of FA hydrogenation commonly involves high temperature (>100 °C) and high H<sub>2</sub> pressure (3–6 MPa) [7–15]. Gowda et al. [7] reported a homogeneous Ru(II) bis(diimine) catalyst for hydrogenating FA into THFA under 130 °C, 5 MPa H<sub>2</sub>, with 99% selectivity. The difficulties encountered in separation and loss of metal centers strongly limit the practical application of homogeneous catalysts [16]. Adkins and Connor [8] in 1931, for the first time reported the hydrogenation of FA using a heterogeneous Cu–Cr catalyst. The reaction was carried out in liquid phase for 11.5 h at 175 °C and 10–15 MPa hydrogen with THFA yield being less than 10%. A higher THFA selectivity of 48% was achieved over a Raney nickel catalyst under modest temperature [9]. Supported

nickel catalysts have been reported to be selective for the synthesis of THFA under very harsh reaction conditions such as 180 °C, 3–4 MPa H<sub>2</sub> and 3.5 h [10–13]. Zhang et al. [14] emphasized the hydrogenation of FA over a series of MnO<sub>x</sub> supported Ru, Pd, Pt and Rh catalysts at 120 °C, 3–6 MPa for 4 h in an aqueous phase and the Ru/MnO<sub>x</sub> showed the best catalytic performance with 79% yield to THFA. Under harsher conditions (220 °C, 3.5 MPa H<sub>2</sub>) the Pd/C catalyst showed full conversion of FA to THFA in isopropanol solvent after 5 h [15]. A main drawback of hydrogenation at high temperature is the possible formation of various by-products, such as 2-methylfuran (MF), tetrahydrofuran, 1, 2-pentanediol and 1, 5-pentanediol [8,9,11–15]. Recently, Khan et al. [17] reported a mild hydrogenation process which described the FA hydrogenation on a hectorite-supported Ru nanoparticles in methanolic solution at 40 °C under a hydrogen pressure of 20 bar and the THFA yield reached 99%. Therefore, selective synthesis of THFA under mild reaction condition is an attractive alternative method to the conventional ones.

In this study we report the successful hydrogenation of FA under ambient conditions catalyzed by a Pd-supported sodium-titanate nanotube catalyst, which shows unprecedented activity and selectivity to THFA at room temperature and 1 bar H<sub>2</sub>. The sodium cations in the titanate are thought to play a crucial role in stabilizing well-dispersed Pd metal particles as well as inhibiting MF formation.

\* Corresponding author. Fax: +86 2132530334.

E-mail address: [yjguan@chem.ecnu.edu.cn](mailto:yjguan@chem.ecnu.edu.cn) (Y. Guan).

## 2. Experimental

### 2.1. Preparation of catalysts

Titanate nanotubes (TNT) were prepared according to the reference [18]. Typically, commercial anatase-type  $\text{TiO}_2$  (2 g) was added to 100 mL of NaOH aqueous solution (10 M). After being stirred for 10 min, the mixture was transferred into a Teflon-lined (120 mL) stainless steel autoclave and statically heated in an oven at  $130^\circ\text{C}$  for 72 h. The white product was filtered and washed with large amount of deionized water until the pH was 7. The final products were subsequently dried at  $110^\circ\text{C}$  overnight, calcined at various temperatures (400, 600 and  $800^\circ\text{C}$ ) for 3 h and labeled as TNT-T (400, 600 and 800, respectively).

For comparison, we also prepared the proton-exchanged TNT with 0.1 M HCl solution to investigate the acid-base properties of TNT samples. After that, the mixture was filtered, washed thoroughly with deionized water and dried at  $110^\circ\text{C}$  and labeled as TNT-H.

Pd supported on commercial anatase-type  $\text{TiO}_2$  or TNTs were prepared using a deposition-reduction method. The support (0.5 g) was dispersed in  $\text{H}_2\text{O}$  (60 mL) with stirring. A specified amount of  $\text{H}_2\text{PdCl}_4$  aqueous solution (21.512  $\text{g}_{\text{Pd}}/\text{L}$ ) was added to the mixture and stirred for 3 h. The final pH value of the suspension was adjusted to 10 by adding NaOH solution (1 M). Then,  $\text{NaBH}_4$  aqueous solution ( $\text{NaBH}_4/\text{Pd} = 10$ , molar ratio) was added into the suspension and the mixture was stirred for another 30 min allowing for the full reduction of  $\text{Pd}^{2+}$  species. Thus obtained catalyst was dried at  $110^\circ\text{C}$  overnight.

### 2.2. Catalyst characterization

Nitrogen adsorption–desorption isotherms at  $-196^\circ\text{C}$  were obtained on a BELSORP-Max equipment. Prior to the measurement, the samples were first degassed at  $150^\circ\text{C}$  under vacuum for 6 h. Specific surface areas (SSA) were calculated according to the Brunauer–Emmett–Teller (BET) method using five relative pressure points in the interval of 0.05–0.30. The pore size distribution was obtained by the BJH model applied to the adsorption isotherm.

Pulse CO chemisorption was performed on a Micromeritics AutoChem 2910 to determine the metal dispersion of the reduced catalysts. Prior to measurement, the catalyst was reduced in a flow of 80 mL/min 10 vol.%  $\text{H}_2$  in Ar at  $80^\circ\text{C}$  for 2 h and then cooled to  $30^\circ\text{C}$  by flushing He for 2 h. Afterwards, CO gas pluses (5 vol.% in He) were introduced in a flow of 110 mL/min. The gas phase CO concentration was followed by thermal conductivity detector (TCD).

The Pd loading was quantified by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. About 5 mg catalysts were digested using 10 mL of aqua regia. The obtained solutions were diluted with deionized water before test.

The power X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) operated at 35 kV and 25 mA. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) images were taken on a FEI Tecnai G<sup>2</sup> F30 microscope operating at 300 kV. The average Pd particle size was calculated by  $d_{\text{TEM}} = (\sum n_i d_i^3) / (\sum n_i d_i^2)$  by measuring at least 100 particles. Temperature-programmed desorption of  $\text{NH}_3$  ( $\text{NH}_3$ -TPD) testing was performed using a TP-5080 chemisorption instrument (Xianquan Co., Ltd., Tianjin, China) with a thermal conductivity detector (TCD). After pretreatment at  $400^\circ\text{C}$  under flowing He (25 mL/min) for 1 h, each sample (100 mg) was cooled to  $100^\circ\text{C}$ , and then adsorbed to saturation by  $\text{NH}_3$  for 30 min. The physisorbed  $\text{NH}_3$  was removed by flushing the sample with He

(25 mL/min) for 1 h at the adsorption temperature.  $\text{NH}_3$  desorption was carried out in the temperature range of  $100$ – $400^\circ\text{C}$  at ramp rate of  $10^\circ\text{C}/\text{min}$ .

Fourier transform infrared (FT-IR) spectroscopy of pyridine adsorption measurements were performed on a Nicolet iS50 spectrometer equipped with a vacuum cell. Catalyst samples were pressed into self-supported disks (12–22 mg with diameter of 13 mm) and activated under vacuum ( $1 \times 10^{-3} \text{ Pa}$ ) at  $350^\circ\text{C}$ . After activation the samples were cooled to room temperature. A spectroscopy of the activated sample was recorded as background. Adsorption of pyridine was conducted at room temperature. Thermo gravimetric analysis (TG) was performed using a NET2SCH STA449F3 TGA analyzer with ramp rate of  $10^\circ\text{C}/\text{min}$  from 25 to  $800^\circ\text{C}$  in  $\text{N}_2$  flow.

X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Kratos AXIS Ultra<sup>DLD</sup> multi-technique X-ray photoelectron spectrometer, equipped with a monochromated Al  $\text{K}\alpha$  radiation ( $E = 1486.6 \text{ eV}$ ). The C 1s peak with binding energy of 284.6 eV was taken as energy reference.

### 2.3. Catalytic tests

A two-necked round-bottom flask was used to carry out the liquid phase hydrogenation of FA. No pretreatment on the catalyst was conducted prior to reaction. The reactor was charged with FA (0.2 mL), solvent (4 mL) and catalyst (50 mg), and the mixture was stirred under ambient hydrogen pressure (balloon) at  $25^\circ\text{C}$  for 1 h. The products were analyzed with flame ionization detector (FID) and capillary column DB-FFAP (30 m length and 0.25 mm internal diameter).

The spent catalyst was recovered by centrifugation washing with ethanol for three times, and then drying in vacuum. The activity of the recovered catalyst was tested under the same conditions as that applied for the fresh sample.

## 3. Results and discussion

### 3.1. Characterization of TNTs

Fig. 1 shows the XRD patterns of the commercial anatase-type  $\text{TiO}_2$  and the TNTs. Diffraction peaks positioned at 9.8, 24 and  $28^\circ$  assigned to the titanates such as  $\text{Na}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$  and  $\text{Na}_2\text{Ti}_3\text{O}_7$  are noticed on TNT (Fig. 1c) [18]. Upon calcination at  $600^\circ\text{C}$ ,

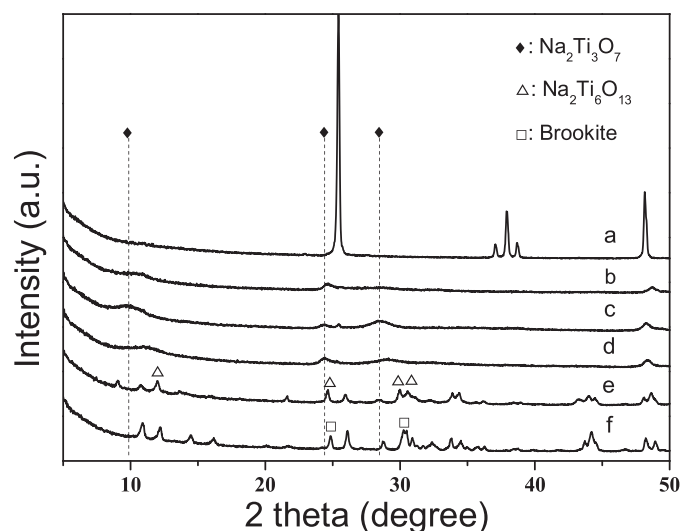


Fig. 1. XRD patterns of pristine anatase and different titanates (TNTs): (a) anatase; (b) TNT-H; (c) TNT; (d) TNT-400; (e) TNT-600; (f) TNT-800.

Download English Version:

<https://daneshyari.com/en/article/39163>

Download Persian Version:

<https://daneshyari.com/article/39163>

[Daneshyari.com](https://daneshyari.com)