



# Highly selective hydrogenation of furfural over supported Pt nanoparticles under mild conditions



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## ABSTRACT

The selective liquid phase hydrogenation of furfural to furfuryl alcohol over Pt nanoparticles supported on SiO<sub>2</sub>, ZnO, γ-Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> is reported under extremely mild conditions. Ambient hydrogen pressure, and temperatures as low as 50 °C are shown sufficient to drive furfural hydrogenation with high conversion and >99% selectivity to furfuryl alcohol. Strong support and solvent dependencies are observed, with methanol and *n*-butanol proving excellent solvents for promoting high furfuryl alcohol yields over uniformly dispersed 4 nm Pt nanoparticles over MgO, CeO<sub>2</sub> and γ-Al<sub>2</sub>O<sub>3</sub>. In contrast, non-polar solvents conferred poor furfural conversion, while ethanol favored acetal by-product formation. Furfural selective hydrogenation can be tuned through controlling the oxide support, reaction solvent and temperature.

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## 1. Introduction

Sustainable low carbon biofuels derived from lignocellulosic or oleochemical biomass sources are urgently sought [1–3] to address climate change and energy security issues arising from the availability of usable versus unburnable [4] non-renewable fossil fuels. The quest for sustainable biofuels also impacts upon the broader chemicals industry, since the overwhelming proportion of carbon feedstocks they employ today obtain from petroleum and natural gas. In this respect, the development of the bio-refinery concept for the co-production of sustainable fuels and chemicals has the power to transform global energy and materials markets, but necessitates the development of new catalytic processes capable of selectively transforming biomass derived oxygenated organics into either alternative 'drop in' chemical intermediates and fuels, or entirely products with novel properties.

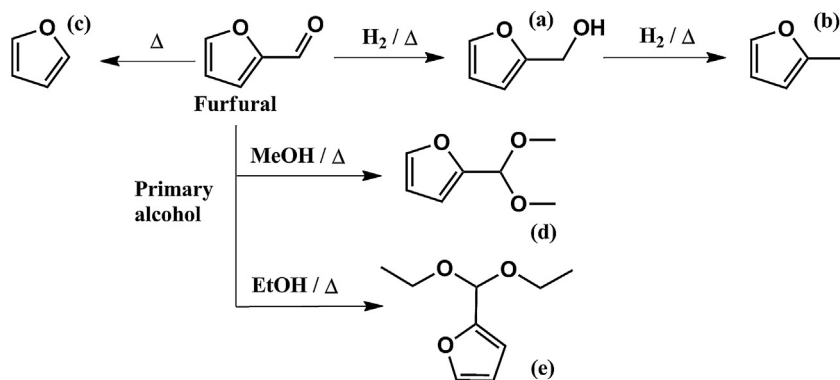
Among these oxygenates, furfural and its derivatives are promising starting materials and building blocks from which to synthesize high volume products such as polyols, which find direct application as monomer precursors for the polyester industry, or

the production of polyamides or polyurethanes via respective oxidation or amination [5,6]. Furfural hydrogenation to furfuryl alcohol, an intermediate to the manufacture of lysine, ascorbic acid and numerous lubricants [7] represents a key synthetic transformation for furfural exploitation (Fig. 1), and one wherein there is significant academic and commercial interest in new energy efficient routes. Approximately 62% of furfural currently produced is converted into furfuryl alcohol [6]. The present industrial process for furfural hydrogenation to furfuryl alcohol employs a copper chromate catalyst [8], operating between 130 and 200 °C, at pressures up to 30 bar. While copper chromate exhibits good activity and selectivity towards furfuryl alcohol, the use of toxic Cr<sub>2</sub>O<sub>3</sub>, whose disposal is prohibited in landfill sites, is highly undesirable, hence the driver for energy efficient alternative catalytic processes operating at mild temperature and pressure and utilizes less toxic components [9–11].

A variety of precious metal catalysts have been investigated for the gas phase and liquid phase hydrogenation of furfural, including Ni, Ru, Pd, Co, Cu and Pt [6,7,12–16]. Platinum in particular has drawn recent attention for the vapor phase hydrogenation of furfural by Somorjai and co-workers [17–19] over SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> mesoporous oxide supports, highlighting the importance of particle size effects; Pt nanoparticles <3 nm favored furfural decarbonylation to furan, whereas those between 3 and

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**Fig. 1.** Furfural reaction scheme containing both hydrogenation and coupling reactions occurring with alcohol based solvents. (a) furfuryl alcohol, (b) methyl furan, (c) furan, (d) 2-furaldehyde dimethyl acetal and (e) 2-furaldehyde diethyl acetal.

7 nm promoted hydrogenation to furfuryl alcohol [13,17]. Sum frequency spectroscopy studies also indicate that metal-support interactions are important for Pt nanoparticles on TiO<sub>2</sub>, facilitating hydrogen spillover and the concomitant formation of a furfuryl-oxy intermediate over titania [18,19]. The influence of surface polarity upon the Pt catalyzed selective hydrogenation of allylic aldehydes was also recently reported over silica supports [20].

Here we investigate the selective hydrogenation of furfural to furfuryl alcohol under extremely mild reaction conditions over Pt nanoparticles supported on SiO<sub>2</sub>, ZnO, γ-Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and MgO. Strong support and solvent dependencies were observed, with methanol and *n*-butanol proving excellent solvents for promoting high furfuryl alcohol yields over uniformly dispersed Pt nanoparticles when using MgO, CeO<sub>2</sub> and γ-Al<sub>2</sub>O<sub>3</sub> as supports at 50 °C and atmospheric hydrogen pressure. In contrast, non-polar solvents conferred poor furfural conversion, while ethanol favored acetal by-product formation, as commonly reported in the literature [12,21–25].

## 2. Experimental

### 2.1. Synthesis

Colloidal Pt nanoparticles were prepared adapting the method of Jones et al. [26], employing a H<sub>2</sub>PtCl<sub>6</sub>·H<sub>2</sub>O precursor since residual chlorine has been found to have a promotional effect in the selective hydrogenation of α,β-unsaturated aldehydes [27]. To a stirred 10 ml aliquot of ethylene glycol (Fisher >99%) at 120 °C, 50 μl of 0.1 M aqueous sodium hydroxide solution was added to promote nucleation. To the hot glycol, a solution of H<sub>2</sub>PtCl<sub>6</sub> × H<sub>2</sub>O (10.6 mM, Alfa Aesar, 99.9%) and polyvinylpyrrolidone (PVP) (91 mM, Alfa Aesar) in a 9:1 per volume ethylene glycol:water mixture was added slowly over the course of an hour resulting in a color change from light brown to black. The reaction mixture was stirred for an additional 20 min and then cooled to room temperature. Nanoparticles were isolated by the addition of acetone (three times the reaction volume) followed by subsequent centrifugation at 3500 rpm. This process was repeated three times and the nanoparticles then dispersed in ethanol before supporting on oxide supports: SiO<sub>2</sub> (Alfa Aesar amorphous fumed, 175–225 m<sup>2</sup> g<sup>-1</sup>); γ-Al<sub>2</sub>O<sub>3</sub> (Alfa Aesar 99.5%, 32–40 m<sup>2</sup> g<sup>-1</sup>), CeO<sub>2</sub> (Alfa Aesar 99.5%, 3 m<sup>2</sup> g<sup>-1</sup>), MgO (Alfa Aesar, 99+%, >7 m<sup>2</sup> g<sup>-1</sup>) and ZnO (Alfa Aesar, 99.9%, 10 m<sup>2</sup> g<sup>-1</sup>). Supports were not pretreated prior to platinum deposition. The resulting slurries were slowly dried in vacuo, and the dried powders then transferred to a tube furnace and heated at 3 °C min<sup>-1</sup> under air (60 cm<sup>3</sup> min<sup>-1</sup>) to 300 °C for 4 h to remove the PVP stabiliser and immobilise the Pt nanoparticles. The result-

ing materials were reduced at 200 °C in flowing 10% H<sub>2</sub>/N<sub>2</sub> for 1 h, cooled and stored in air.

### 2.2. Characterization of catalysts

All samples were analysed via a JEOL 2010 Transmission Electron Microscopy (TEM) operated at 200 kV, with STEM were recorded using a C<sub>s</sub> aberration-corrected JEOL 2100F microscope at 200 kV. Images were collected using a Gatan Ultrascan 4000 digital camera operated by Digital Micrograph software. Samples were dispersed in ethanol and deposited on 300-mesh carbon-supported copper grids and dried under ambient conditions. Metal contents were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer Optical Emission Spectrometer Optima 5300 DV) after microwave digestion of the samples in 2 ml HNO<sub>3</sub> (Romil SPA grade 70%), 2 ml HCl (Romil SPA grade 60%), and depending on the oxide, 2 ml HF (Romil SPA grade 40%) at 200 °C (CEM-MARS microwave reactor) followed by aqueous dilution. Bulk compositions are ±10%. BET surface areas were determined via N<sub>2</sub> physisorption using a Micromeritics TriStar porosimeter. X-ray photoelectron spectra were acquired on a Kratos AXIS HSi spectrometer equipped with a charge neutralizer and monochromated Al Kα excitation source (1486.7 eV), with energies referenced to adventitious carbon at 284.6 eV. Spectral fitting was performed using CasaXPS version 2.3.15. Powder X-ray diffraction was performed on a Bruker D8 Advance diffractometer using monochromated Cu Kα<sub>1</sub> radiation (λ = 0.1542 nm). Subsequent peak assignment was based on the ICDD's PDF-2 2012 database.

### 2.3. Catalytic testing

Catalytic hydrogenation was performed using a 12-port Radleys Plus Reaction Station. Reaction tubes were first evacuated and purged with hydrogen (Energas 99.99%) three times to ensure that the system was air-free; hydrogen was supplied via balloons pressurised to 1.02 atm, as measured by a Measurement Specialties™ XP5 pressure sensor. In a typical run, 10 ml of solvent, 16.5 μl (approximately 0.02 mmols) of furfural and 20 mg of catalyst were mixed at 600 rpm. The reaction mixture was sampled at measured time intervals with quantification via an external dodecane standard and analysis on a Bruker Scion 456-GC equipped with a flame ionisation detector and a Zebtron ZB-5 (5%-phenyl-95%-dimethylpolysiloxane) capillary column. GC-MS was performed using an Agilent 6890 GC equipped with an Agilent 5973N Quadrupole mass spectrometer and an RXI-5MS (5%-phenyl-95%-dimethylpolysiloxane) capillary column. Product selectivity was determined according to Eq. S1, with carbon mass

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