



## Selective hydrogenation of citral to 3,7-dimethyloctanal over activated carbon supported nano-palladium under atmospheric pressure



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### HIGHLIGHTS

- Selective hydrogenation of citral into 3,7-dimethyloctanal was developed.
- 1 wt.% Pd/C catalyst showed the highest catalytic activity and selectivity.
- Citral conversion of 100% and 3,7-dimethyloctanal selectivity of 96% were obtained.

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### ABSTRACT

Hydrogenation of citral was studied over activated carbon supported Pd nanoparticles (Pd/C catalyst) under atmospheric pressure. Pd/C catalysts were prepared using glucose as a stabilizer and characterized by several techniques such as ultraviolet–visible absorption spectroscopy (UV–Vis), transmission electron microscopy (TEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). 1 wt.% Pd/C catalyst showed high catalytic activity for the hydrogenation of citral to 3,7-dimethyloctanal with high selectivity. A study on the optimization of the reaction conditions such as the reaction temperature and reaction solvent has been performed. Under optimal experimental conditions, citral conversion of 100% and 3,7-dimethyloctanal selectivity of 96% were obtained after 4 h at 303 K under atmospheric H<sub>2</sub> pressure.

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## 1. Introduction

Selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes is a reaction of great importance in the synthesis of fine chemicals [1,2]. Citral belongs to this class of compounds and it is valuable in chemical industry [3–6]. Citral contains three double bonds. Two of them are conjugated C=O and C=C bonds, and the third is isolated C=C bond. Hydrogenation of citral can generate several valuable products such as citronellal, geraniol, nerol and citronellol. Therefore, the real challenge in citral hydrogenation is the differentiation between hydrogenation of the different double bonds leading to either citronellal, 3,7-dimethyloctanal, 3,7-dimethyl-2-octenal, 3,7-dimethyl-2-octenol or 3,7-dimethyloctanol.

Many factors influence the product selectivity, such as the metal type, metal particle size and morphology, the use of second metal, and properties of the support [7–11]. It is reported that the Pd based catalysts generally possible to suppress C=O hydrogenation almost completely, provided that harsh reaction conditions (high pressure, high temperature) are avoided [12]. The hydrogenation of citral over Pd based catalysts usually cannot selectively reduce one of the two bonds. As one of the important hydrogenation of citral products, citronellal is obtained by the selective hydrogenation of the conjugate “C=C” bonds. Thus, the challenge with Pd is the maximization of the yield of citronellal.

Compared with citronellal, the synthesis of 3,7-dimethyloctanal is generally of less importance. However, it is also a very important synthetic intermediate in organic chemistry and is valuable in the production of biological and food-related materials such as insect sex hormone [5]. Synthesis of 3,7-dimethyloctanal has been early studied using homogenous catalyst such as water soluble palladium complex [12]. Although homogeneous catalysts usually show

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high catalytic activity, they are difficult to be recycled. The use of solid catalysts is more environmentally friendly and easier to separate and reuse than their homogeneous counterparts [13,14]. Metal nanoparticles-based solid catalysts, particularly those that have well-defined size/shape, have attracted increasing research attention for catalytic applications. Various metal catalysts supported on inorganic supports have been used as solid catalysts for the hydrogenation of citral in liquid phase and vapor phase [15,16]. But the activity or selectivity to form 3,7-dimethyloctanal was not considered satisfactory for some metal catalysts. In addition, some of the catalytic systems were carried out under severe reaction conditions such as high reaction temperature and high reaction pressure. Palladium based solid catalysts were found to be active for citral hydrogenation, and it is more selective to C=C bond hydrogenation, affording citronellal and 3,7-dimethyloctanal in good yields [10]. Besides the active metal sites, the selectivity of citral hydrogenation can also be improved by the use of an appropriate supports [17]. Compared with other oxides supports, activated carbon (AC) have several advantages such as inert property, high BET surface area and developed porosity [18]. Carbon supported Pd nanoparticles have been extensively used in many chemical reactions, especially for hydrogenation reaction. However, the Pd nanoparticles tend to aggregate to form large-size particles, resulting in the decrease of the catalytic activity. Generally, the use of an appropriate stabilizer can prevent Pd nanoparticles from aggregation, thus keep the activity of Pd nanoparticles stable. Various nitrogen-containing organic polymers or simple compounds such as polyvinylpyrrolidone [19], polyvinylidene fluoride [20], and *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl) ammonium chloride salt [21] were used to stabilize Pd nanoparticles. However, the cost of these stabilizers is high and the waste is dangerous or potentially harmful to the environment. Therefore, it is necessary to develop a new method for the synthesis of Pd/C catalyst using cheap and safe stabilizer, and show high catalytic activity and selectivity for the hydrogenation of citral.

Glucose is renewable resource, which can be obtained from biomass [22]. It poses no threat to the environment. According to safety data sheet, it is considered as a safe substance and characterized by good biodegradability, so there is no danger of the accumulation of glucose in the environment. It is also known as chemical capping, and can be used to passivate the surface of the particles so that the particles do not agglomerate or ripen to form larger particles [23]. This ensures that the synthesized nanoparticles are stable with uniform size distribution. Besides its environmental safety, glucose is cheaper than the common stabilizer. For example, the price of glucose (Aldrich) is 38.6 \$/kg, while the price of the most common stabilizer Polyvinylpyrrolidone (PVP) with average mol wt 40,000 from Aldrich is 254 \$/kg. Herein, glucose was chose as a stabilizer for the synthesis of active carbon supported Pd nanoparticles, and the as-prepared Pd/C catalysts were used for the hydrogenation of citral to 3,7-dimethyloctanal.

## 2. Experimental

### 2.1. Materials

Citral (96.7%) with E/Z ratio of 1:1 was purchased from Sinopharm Chemical Reagent (Shanghai, China) and purified by distillation before use. Palladium(II) chloride (PdCl<sub>2</sub>, 98%) and active carbon were provided by Chenzhou Gao Xin Platinum Co., Ltd. (Chengzhou, China). Ethanol (≥99.5%), sodium borohydride (NaBH<sub>4</sub>, 98%), Hydrochloric acid (HCl, 36–38 wt.%) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai China). Methanol (≥99.5%), tert-Butyl alcohol (≥99.0%), isopropanol and 1-propanol were purchased

from Tianjin Fu Chen Chemical Reagent Co., Ltd. (Tianjin China). Glucose was purchased from Glucose was purchased from Sinopharm Chemical Reagent (Shanghai, China).

### 2.2. Catalyst preparation

#### 2.2.1. Synthesis of Pd colloids

Pd colloids were prepared according to the known procedures with some slight modifications [21]. Typically, PdCl<sub>2</sub> (1.77 mg, 10 mmol) was firstly dissolved in 2 M HCl (5 mL) with a magnetic stirring for 15 min. Then an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (15 wt.%) was added dropwise until the solution pH reached 7.0. A mixed solution of NaBH<sub>4</sub> (0.01 mmol in 1 mL) and glucose (0.34 mmol in 1 mL) were added dropwise into the above mixture under vigorously stirring. After addition, the resultant mixture was stirred for another 20 min, and Pd colloids were obtained as dark-brown homogeneous solutions.

#### 2.2.2. Preparation of Pd/C catalysts

Pd/C catalysts with the Pd weight percentage (wt.%) from 0.5 to 3.0 were prepared by incipient wetness impregnation method. Typically, active carbon (0.6 g, S<sub>BET</sub> = 1318 m<sup>2</sup> g<sup>-1</sup>) was added into an appropriate amount of the as-prepared Pd colloidal solution (120 mL), and then the mixture was stirred vigorously at 333 K for 1 h. After impregnation and the sample was dried at 90 °C for 8 h to yield a black powder Pd/C catalyst. The Pd content was determined by ICP-AES (Table 1).

### 2.3. Catalyst characterization

The BET surface areas (S<sub>BET</sub>) of the support and the catalysts were evaluated from the N<sub>2</sub> adsorption–desorption at –196 °C using a TriStar 3000 apparatus. The samples were degassed under 1.33 × 10<sup>-7</sup> Pa at 353 K overnight before measurements. UV–Vis absorption spectroscopy was conducted on a Perkin Elmer Lambda 17 UV–Vis spectrophotometer with a scan range of 190–900 nm and an optical path length of 1.0 cm. TEM micrographs were characterized by transmission electron microscopy by means of a JEOL-1230, operating at 100 KV. Samples were prepared by placing a drop of glucose Pd sol or a droplet of well-homogenized heterogeneous Pd/C catalyst on a carbon film supported by a copper grid and subsequently drying at ambient conditions. Raman spectra were measured using a DXRMicro-Raman Spectroscopy System (Thermo Fisher Scientific) with a laser excitation wavelength of 780 nm. The as-prepared samples were excited with 5 mw Raman laser power five times each for 2 s. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo VG scientific ESCA Multi-Lab-2000 spectrometer with a monochromatized Al Kα source (1486.6 eV) at constant analyzer pass energy of 25 eV. The binding energy was estimated to be accurate within 0.2 eV. All binding energies (BEs) were corrected referencing to the C1s (284.6 eV) peak of the contamination carbon as an internal standard.

**Table 1**  
The Pd content and the text structure of the prepared Pd/C catalysts.

Entry	Catalysts	Pd (%)	V <sub>p</sub> (cm <sup>3</sup> g <sup>-1</sup> )	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )
1	C	–	0.34	1318
2	0.5 wt% Pd/C	0.49	0.33	1252
3	1.0 wt% Pd/C	0.99	0.32	1213
4	2.0 wt% Pd/C	2.00	0.31	1144
5	3.0 wt% Pd/C	2.98	0.31	1145

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