



# The critical role of CeO<sub>2</sub> crystal-plane in controlling Pt chemical states on the hydrogenolysis of furfuryl alcohol to 1,2-pentanediol



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## ABSTRACT

1,2-pentanediol (1,2-PeD), as a valuable chemicals, can be obtained from the hydrogenolysis of furfural or furfuryl alcohol, but its high and selective synthesis is still challenging. Here, we report the production of 1,2-PeD from furfuryl alcohol over various fine-shaped Pt/CeO<sub>2</sub> catalyst and their structure-property relationships. The yield of 1,2-PeD can reach 77% over Pt/CeO<sub>2</sub>-nanocube, which is the highest among reported catalysts; but the yield is low over Pt/CeO<sub>2</sub> nanorods (48.5%). Extensive characterizations reveal that the chemical state of Pt plays key role in the selective production of 1,2-PeD, which is controlled by the surface oxygen vacancies of CeO<sub>2</sub> through metal-support interaction. CeO<sub>2</sub>-nanocube exposed (1 0 0) facet has suitable interaction with Pt (abundant metallic Pt species and small particle size) and therefore results in the best catalytic performance. This work highlights the importance of optimizing the ceria terminal facets in rationally tuning Pt surface states in Pt/CeO<sub>2</sub> systems for selective production of 1,2-PeD.

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## 1. Introduction

Nowadays, the hydrogenation/hydrogenolysis of biomass-based furfural (FA) or furfuryl alcohol (FFA) to high value-added alcohols or polyols has attracted great attention [1–9]. 1,2-pentanediol (1,2-PeD), as one of the most valuable FFA hydrogenolysis products, is widely applied in cosmetic industry or as a key intermediate of low-toxic microbicides [5]. Therefore, its direct production from FA/FFA under mild conditions has been subject to many active studies.

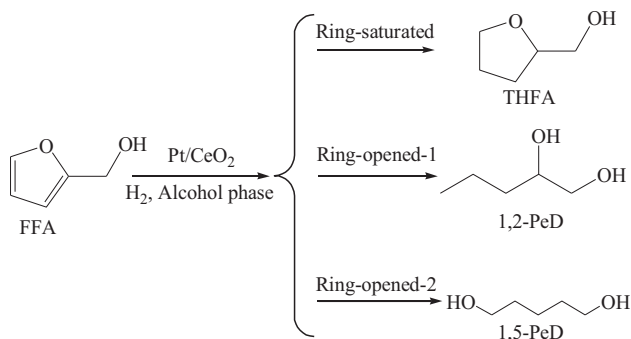
As early as 1930s, CuCr<sub>2</sub>O<sub>4</sub> catalytic systems were found to be active in the direct hydrogenolysis of FA/FFA to pentanediols [10]; however, the existence of Cr in catalysts can cause serious environmental problems, which is not ideal for the modern society. Some fundamental studies in improving this reaction have been reported in recent years [5–8]. For example, a Ru/MnO<sub>x</sub> system was established and a maximum yield of 42% 1,2-PeD was obtained [5], but the yield of the target product and the stability of this catalytic system are still unsatisfactory. The Mg–Al hydrotalcite-supported Pt catalytic system was also developed with 73% yield of 1,2-PeD from furfural [6], but its large-scale

application with good stability is still a challenge [11–13]. Some non-precious metal catalytic systems were also developed. For example, Cu-based systems at relatively harsher reaction conditions were also exploited in recent years; however, the selectivity to 1,2-PeD in those systems still cannot meet the application requirements (lower than 55%) [14,15]. Recently, we found that Pt/CeO<sub>2</sub> is excellent for the hydrogenolysis of FA/FFA, with good yields of 1,2-PeD in aqueous phase and green alcohol solvents at 65.5 and 59.9% respectively [7,8]. More importantly, the Pt–CeO<sub>2</sub> catalytic system has an admirable durability in alcohol phases, which points to its potential industrial applications [8]. However, the detailed investigation about the roles of Pt and CeO<sub>2</sub> in the direct hydrogenolysis of FFA is still lacking, which is necessary for the further improvement of 1,2-PeD selectivity.

It is well known that CeO<sub>2</sub> is an excellent catalyst or promoter in a large number of reactions [16,17]. Moreover, crystal orientations of CeO<sub>2</sub> have been proven to play an important role on the activity and selectivity in a series of reactions [18–21]. For example, different shaped ceria nanocrystals showed significantly different selectivities for ethanol oxidation [19]; also, the activity of C<sub>2</sub>H<sub>2</sub> hydrogenation and CO oxidation was found to be ceria-shape-dependent [20]. For CeO<sub>2</sub> supported metal catalysts, the strong metal-support interaction (SMSI) is often observed [22–26], which can dramatically promote the rate, and more importantly, tune the pathways of some reactions [25]. For instance,

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**Scheme 1.** The reaction routes of the direct FFA hydrogenation/hydrogenolysis over Pt/CeO<sub>2</sub> catalytic systems.

the effect of CeO<sub>2</sub> crystal plane on the activity of Au/CeO<sub>2</sub> in the water gas shift reaction was reported [24]; Pd/CeO<sub>2</sub> catalysts with different ceria crystal planes were found to exhibit totally different activities for CO and propane oxidation [27]; shaped Pt/CeO<sub>2</sub> catalysts showed dramatically different activities in quinolines hydrogenation [26]. Moreover, Ir/CeO<sub>2</sub> catalytic systems with different Ir contents were proved to have different chemical states, which is induced by SMSI effect, and dramatically affects the reaction pathways of CO<sub>2</sub> hydrogenation [25].

In the hydrogenolysis of FA/FFA over Pt/CeO<sub>2</sub> catalytic systems, there are two competitive pathways: furan ring opening and saturation (Scheme 1), which lead to different products, namely, 1,2-PeD/1,5-PeD or tetrahydrofurfuryl alcohol (THFA). We aim to utilize the CeO<sub>2</sub> morphological effect and optimize the interaction between loaded Pt and ceria to enhance the selectivity of 1,2-PeD in the direct FA/FFA hydrogenolysis. Previous studies [7,8] illustrated that FFA is firstly obtained during the hydrogenolysis of FA to 1,2-PeD, so we choose FFA as the substrate to simplify the investigation in this work.

Herein, CeO<sub>2</sub> nanocrystals with different morphologies (nanorod, nanocube and octahedron) were used to load Pt, and their effect in FFA hydrogenation/hydrogenolysis was investigated from a microscopic view. It is found that the chemical state of supported Pt species can be tuned by the exposed planes of the CeO<sub>2</sub>, which leads to significantly different selectivities to 1,2-PeD during the FFA hydrogenolysis. A 77% yield of 1,2-PeD (the total pentanediol yield up to 84%) was achieved over CeO<sub>2</sub> nanocubes supported Pt catalyst, which is at the highest level till now. This study provides a first step to the detailed understanding of the direct hydrogenolysis of furan rings over excellent Pt-based CeO<sub>2</sub> catalytic systems.

## 2. Experimental section

### 2.1. Catalyst preparation

Ceria nanorods (CeO<sub>2</sub>-R) and nanocubes (CeO<sub>2</sub>-C) were prepared by the hydrolysis of Ce (III) ions in a condensed NaOH solution, followed by a hydrothermal treatment [28]. Typically, 1.736 g Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 19.2 g NaOH were dissolved in 10 and 70 mL of deionized water, respectively. After the mixing of two solutions, the mixture was kept stirring for another 30 min. Then, the sealed Teflon bottle with suspension was placed in a stainless steel autoclave, and hydrothermally treated at 100 °C and 180 °C for 24 h to obtain the ceria nanorods and ceria cubes, respectively. The formed solids were separated by filtration and washed by deionized water until the pH of the filtrate is close to 7, followed by drying at 100 °C for 12 h and calcining at 500 °C for 3 h in air.

For the synthesis of ceria octahedron (CeO<sub>2</sub>-O) [29], 0.858 g Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 0.0076 g Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O were firstly dissolved in 10 and 70 mL of deionized water, respectively. Then, these two solutions were mixed together, and stirred for another 30 min. After sealing the Teflon bottle in a stainless steel autoclave, the mixture were heated at 170 °C for 10 h. The gained solids were separated by centrifugation and washed by deionized water and methanol for several times. The samples were dried at 100 °C for 12 h, followed by calcining at 500 °C for 3 h in air.

All Pt/CeO<sub>2</sub> samples are prepared by incipient wetness impregnation method. Typically, an aqueous solution of Pt(NO<sub>3</sub>)<sub>2</sub> was mixed with CeO<sub>2</sub> supports and stirred to get a slurry. The slurry was dried at 50 °C for 12 h, and 100 °C for another 12 h. Then the solids were calcined at 500 °C for 3 h, and labeled as n%PtO<sub>x</sub>/CeO<sub>2</sub>-M (n is the Pt loading amount and M denotes the ceria morphology). Before use, the catalysts were reduced at 300 °C for 2 h under 10% H<sub>2</sub>-Ar mixed gas, and labeled as n%Pt/CeO<sub>2</sub>-M. The Pt loading in catalysts was confirmed by inductively coupled plasma atomic emission spectrometry (ICP-AES).

### 2.2. Catalysts activity tests

The hydrogenolysis of furfuryl alcohol was conducted in a Teflon-lined stainless-steel autoclave (50 mL). After sealing the desired dosage of FFA, catalyst and solvent in the reactor, the autoclave was purged with H<sub>2</sub> three times and pressurized to the desired pressure. Then, the autoclave was heated to the predetermined temperature in a short time. After reaction, the reactor was quenched in an ice-water bath immediately.

The liquid phase was separated from the catalyst by centrifugation, and two individual GC/MS systems were used for product analyses. The qualitative analysis of products was carried out on a GC-MS system (Agilent 7890A-5975C), and the quantitative analysis was executed on a GC system (Agilent 7890B) equipped with an HP-5 column and an FID detector.

### 2.3. Catalyst characterization

The synthesized Pt/CeO<sub>2</sub> catalysts were characterized extensively to full understand the structure-property relationships of the catalytic system.

Powder X-ray diffraction (XRD) patterns were recorded in the  $\theta$ - $2\theta$  mode on a D8 Focus diffractometer (CuK $\alpha$ 1 radiation,  $k = 1.5406$  Å), operated at 40 kV and 40 mA within scattering angles of 10–80°. Nitrogen sorption measurements were performed on a Micromeritics ASAP 2020M sorption analyzer. The samples were degassed at 200 °C for 6 h, and measured at –196 °C. The Brunauer-Emmett-Teller (BET) method was adopted to calculate the specific surface area. Chemical analysis of samples was performed by an Agilent 725ES inductively coupled plasma atomic emission spectrometry (ICP-AES). Scanning electron microscopy (SEM) images of samples were recorded on a Nova NanoSEM 450 microscopy at 3 kV. Transmission electron microscopy (TEM) images of samples were obtained on a JEOL Model 2100F electron microscopy at 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Scientific Escalab 250 Xi system with monochromatic Al K $\alpha$  radiation, and the results were calibrated using the C 1s peak at 284.6 eV. The Raman spectra were obtained on a Renishaw inVia Reflex spectrometer under ambient conditions, and the 532 nm line of a Spectra Physics Ar<sup>+</sup> laser was used for the excitation. The CO-pulse adsorption was performed at 25 °C (CO:Pt = 1:1) on a Micromeritics AutoChem II 2920 system. Diffuse reflectance infrared Fourier transform spectra (DRIFTS) of CO-adsorption were recorded on a Nicolet Model iS-50 FT-IR spectrometer equipped with an MCT/A detector, and the sample cell was fitted with ZnSe windows. The FT-IR spectra of

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