



Short communication

# Biosynthesis of ruthenium nanoparticles supported on nitric acid modified activated carbon for liquid-phase hydrogenation of 2,2,4,4-tetramethylcyclobutane-1,3-dione



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## ABSTRACT

A plenty of uniform and spherical ruthenium nanoparticles were prepared by the adsorption–bioreduction method using the *Cacumen Platycladi* extract and supported on the activated carbon which was modified with nitric acid. The catalytic performance of as-prepared Ru/AC–HNO<sub>3</sub> catalysts was investigated in the liquid phase hydrogenation of 2,2,4,4-tetramethylcyclobutane-1,3-dione to 2,2,4,4-tetramethylcyclobutane-1,3-diol. Different characterization techniques of BET, XRD, TEM, and FTIR were applied to understand the origin of the catalytic activity. With a comprehensive analysis of the experimental results, we can draw a conclusion that the higher dispersion of ruthenium nanoparticles and the smaller particle size give rise to the results which indicate a remarkable enhancement of the catalytic performance in comparison with the non-modified AC samples.

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## 1. Introduction

2,2,4,4-tetramethylcyclobutane-1,3-diol (CBDO) can be a versatile chemical intermediate with a huge market demand for producing many useful platform polymeric materials. For example, compared with the conventional products, polyesters synthesized from CBDO and dicarboxylic acid will have higher glass transition temperature, impact strength, weatherability and hydrolytic stability [1]. More recently, Eastman's novel Tritan™ copolyester was introduced in 2007 as a polymer produced from dimethyl terephthalate (DMT), 1,4-cyclohexanedimethanol (CHDM) and CBDO in various ratios. Tritan™ has emerged as a possible substitute of traditional polycarbonate polymer, to be used as new plastics in the packaging industry [2]. Nowadays, CBDO is produced in industry from the catalytic hydrogenation of the corresponding 2,2,4,4-tetramethylcyclobutane-1,3-dione (TMCB), as shown in Fig. 1 [3,4]. Hydrogenation of TMCB has been carried out in both homogeneous and heterogeneous systems based on Ru catalysts or Raney nickel catalysts, but the catalyst activity currently remains low [5]. Therefore, research and development of more efficient catalyst are still in great demand.

As an important industrial carbonaceous material, activated carbon (AC) has many applications in filtration, purification and could be used as an ideally shaped substrate for noble metals [6–9]. The superiority of AC lies in its high surface area and well-developed internal pore structure. Unfortunately, the hydrophobic and apolar property restrict

its large scale usage. So the modification of carbon surface is urgently needed to obtain a more hydrophilic surface structure associated with more presence of oxygen containing groups. In general, various reagents such as nitric or sulfuric acid, potassium permanganate, hydrogen peroxide and ozone-based gas are frequently used in the process to transform the AC to more polar materials [10].

In the last decade, biosynthesis of metal nanoparticles using biological plants and microorganisms has intrigued intensive research interest [11,12]. Compared with the traditional physical and chemical synthetic strategies, this simple and eco-friendly plant-mediated strategy appears to be more promising in preparation of efficient catalysts [13,14]. The present investigation highlights the benefit of biosynthesis (using *Cacumen Platycladi* (CP) leaf extract) ruthenium nanoparticles supported on surface modification AC samples and probes the catalytic activity of as-synthesized catalysts in the hydrogenation of TMCB to CBDO.

## 2. Experimental section

## 2.1. Catalyst synthesis

To prepare the CP extract, 2 g milled CP leaf were added to 100 mL sterile water in a 250 mL shaker at 60 °C for 4 h. The concentration of this CP extract was denoted as 10 g/L and used for the subsequent catalyst preparation. The surface modification of AC samples was performed by using 1 mol/L diluted nitric acid [10]. 1.4 g of the AC was refluxed in 50 mL HNO<sub>3</sub> solution for 2.5 h near its boiling temperature of 85 °C. The modified AC was washed thoroughly with deionized water until neutral pH and dried overnight at 60 °C.

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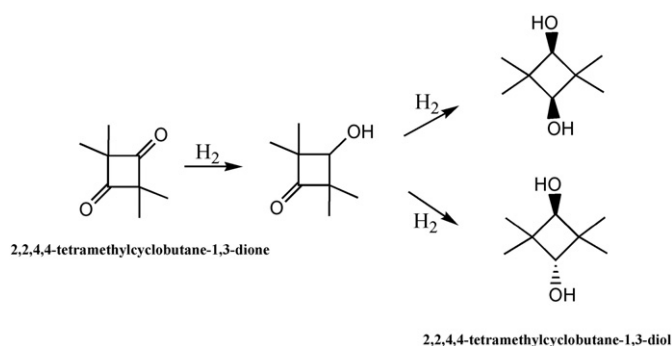


Fig. 1. Reaction pathway of the hydrogenation of TMCB.

Table 1

Textural properties of the supports and catalysts.

Sample	Surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ )	Total pore volume ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	Mesopore volume ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	Average pore size (nm)
AC	872	0.83	0.61	5.5
1 wt.% Ru/AC	806	0.75	0.52	4.8
2 wt.% Ru/AC	731	0.60	0.43	4.5
AC-HNO <sub>3</sub>	819	0.64	0.43	4.2
1 wt.% Ru/AC-HNO <sub>3</sub>	803	0.65	0.44	4.3
2 wt.% Ru/AC-HNO <sub>3</sub>	785	0.69	0.51	4.7

The Ru-based catalyst was prepared by the adsorption–bioreduction method using the as-prepared CP extract [13,15–17]. 0.6 g modified AC was impregnated with an aqueous RuCl<sub>3</sub> solution (50 mL, 2.3 mmol/L)

in a water bath at 60 °C for 1 h. Then 30 mL CP extract were slowly added to the solution and stirred for another 5 h. After that, the suspension was filtered, washed and dried overnight at 60 °C in vacuum and calcined under N<sub>2</sub> at 500 °C for 3 h. For comparison, other Rh, Pt, and Pd-based catalysts were prepared by adopting the same procedure by substituting the RuCl<sub>3</sub> solution by RhCl<sub>3</sub>, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and PdCl<sub>2</sub>, respectively. The loadings of the noble metal were all 2.0 wt.%.

## 2.2. Catalyst characterization

Textural parameters have been calculated from the nitrogen adsorption–desorption isotherms at –196 °C with a Micromeritics ASAP 2020 analyzer. The accurate chemical composition of each sample was determined by inductively coupled plasma atomic mass spectrometry using a Thermo Fisher Scientific ICP-MS XSeries II. And the X-ray diffraction (XRD) analysis was conducted by a Shimadzu powder X-ray diffractometer. The radiation source was monochromatized CuK $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) at a tube voltage of 40 kV and a current of 30 mA. Transmission electron micrographs (TEM), high resolution transmission electron microscope (HRTEM), and energy-dispersive X-ray spectroscopy (EDS) were captured on a FEI Tecnai G2 F20 with a field emission electron gun source and operated at 200 kV and with an extracting voltage of 4.5 kV. Fourier Transform Infrared Spectroscopic (FTIR) studies were collected by a Nicolet 5700 FTIR infrared spectrometer, where the samples were ground with KBr and pressed into thin wafer.

## 2.3. Catalyst evaluation

Liquid phase catalytic hydrogenation of TMCB was performed in a stainless steel batch reactor (SS-316, 100 mL) with a magnetically stirrer at the speed of 500 rpm. Typically the reactor was charged with TMCB dissolved in 5 mL tetrahydrofuran (5 wt.%) and the biosynthesis

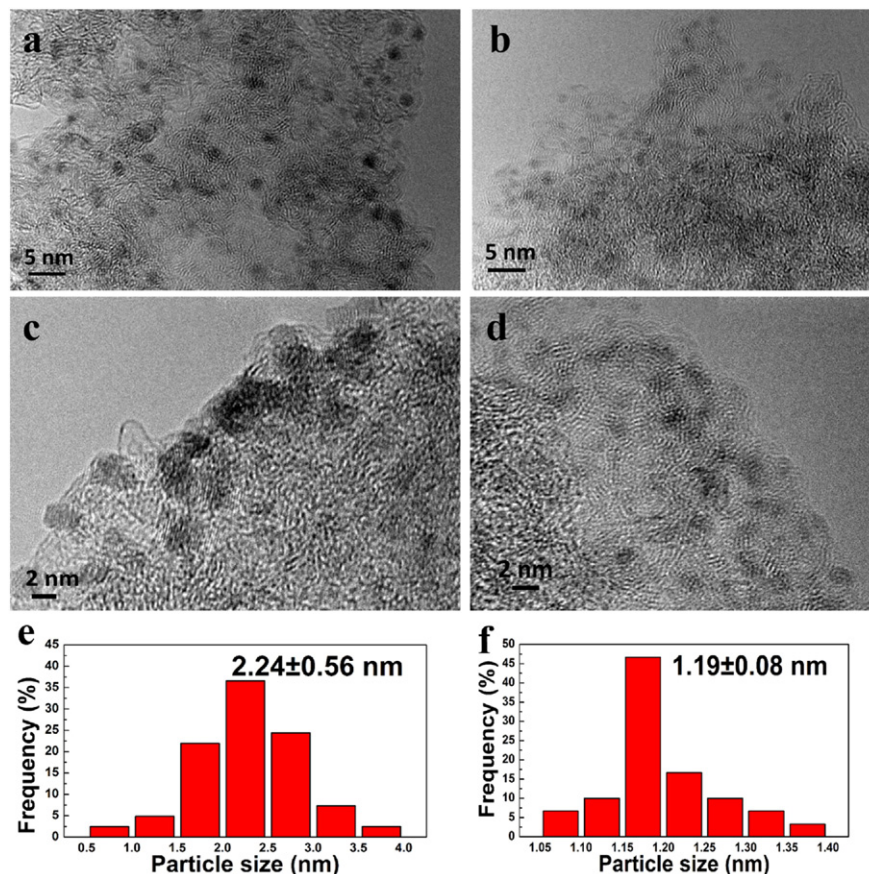


Fig. 2. Representative TEM images of the samples, (a,c) 2 wt.% Ru/AC, (b,d) 2 wt.% Ru/AC-HNO<sub>3</sub> and the size distributions of the samples, (e) 2 wt.% Ru/AC, (f) 2 wt.% Ru/AC-HNO<sub>3</sub>.

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