



A sustainable process for the production of 2-methyl-1,4-butanediol by hydrogenation of biomass-derived itaconic acid



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ABSTRACT

Pd–ReO_x/C catalysts with different Re contents were prepared and employed to catalyze the aqueous hydrogenation of itaconic acid in this study. The Pd–ReO_x/C catalysts were characterized by XRD, TEM, BET, NH₃-TPD and H₂-TPR. Results showed that the addition of ReO_x species in supported Pd catalysts promoted the direct conversion of itaconic acid to 2-methyl-1,4-butanediol. The promoting effect was ascribed to the interaction between Pd and ReO_x species, as has been proved by the characterizations. A 2-methyl-1,4-butanediol yield of above 80% could be obtained over Pd–3ReO_x/C under the reaction condition of 180 °C, 4 MPa H₂.

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1. Introduction

Biomass is recognized as the most abundant carbon resources and the utilization of this renewable resources for fuel and chemical production offers the advantage of reduction of environmental burdens [1–4]. The issues of energy crisis and environmental pollution people confronted currently could be solved in this way in many researchers' opinion [5]. Therefore, the valorization of the biomass and biomass-derived molecules has attracted intensive attention worldwide. Itaconic acid (IA), which was selected as one of the top platform molecules by the US Department of Energy [6], could be converted into methyl- γ -butyrolactones (MGBLs) and 2-methyl-1,4-butanediol (MBDO) via hydrogenation. These are all value-added chemicals widely applied in the pharmaceutical industry and the polyester industry [7].

Previous reports showed that IA hydrogenation first produced MGBLs, and the further hydrogenolysis of MGBLs resulted in MBDO formation [8]. Currently, investigations on direct IA hydrogenation to MBDO mainly focused on homogeneous catalysts. Ru catalysts with different ligands, additives and reaction mediums could adjust the product distribution in Geilen et al.'s research [8]. However, the drawbacks in the catalyst recovery restricted the application of these homogeneous catalysts. Heterogeneous catalysts such as

Ru/TiO₂ and Pd/C were also found to be efficient in IA hydrogenation to produce MGBLs. Primo et al. reported that MGBLs could be produced as the main products (90% yield) over Ru/TiO₂ under the condition of 150 °C, 3.5 MPa H₂ [9]. In our previous work, we found that Pd catalysts supported on functionalized active carbon were efficient in IA hydrogenation to produce MGBLs (nearly 90% yield) [10]. To date, few studies have focused on the one-pot transformation of IA to MBDO. Considering the various advantages that heterogeneous catalysts possessed [1], the rational design and fabrication of highly efficient heterogeneous catalysts capable of direct conversion of IA to MBDO are urgent.

Analogous to the IA, succinic acid (SA) is another important dicarboxylic acid which could also be produced from biomass fermentation [11]. SA hydrogenation also underwent hydrogenation and intramolecular dehydration to form γ -butyrolactone (GBL), and subsequent GBL hydrogenolysis could generate 1,4-butanediol (BDO) [12]. Until now, a lot of catalysts have been developed to catalyze SA hydrogenation. Monometallic Pd- and Ru-based catalysts were found to be efficient in SA hydrogenation to produce GBL [13–15]. Nonetheless, bimetallic catalytic system was generally necessary to obtain BDO. Among them, bimetallic Pd–Re [16] and Pd–Fe [12] catalysts were found to be efficient. Inspired by this, ReO_x promoted Pd/C catalysts with different Re contents were employed in this research and direct conversion of IA to MBDO was achieved over heterogeneous Pd–ReO_x/C catalysts for the first time. It was found that the interaction existed between Pd and ReO_x species was the motive for the efficient IA hydrogenation to

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MBDO in one pot. An MBDO yield of 80% could be obtained over Pd-3ReO_x/C catalyst under relatively mild conditions of 180 °C, 4 MPa H₂ and 6 h.

2. Material and methods

2.1. Materials

IA and hydrochloric acid were provided by Sinopharm Chemical Reagent Co., Ltd. 2-MGBL, MBDO, PdCl₂ and NH₄ReO₄ were bought from Sigma Aldrich Chemicals. Commercially available coconut shell-based active carbon was purchased from Fujian Xinsen Co., Ltd. All the reagents were used without any further purification.

2.2. Catalyst preparation

Catalysts used in this study were prepared by incipient-wetness impregnation. In a typical procedure, PdCl₂ and NH₄ReO₄ were first dissolved in the appropriate amount of HCl solution, after which ammonia solution was used to adjust the pH of the solution to 4.0. Then, under vigorous agitation, active carbon which was pretreated by 13 wt% HNO₃ at 75 °C was added to the mixture. The mixture was then placed at room temperature for 24 h. The catalyst was dried overnight at 100 °C. Afterwards, it was reduced at 300 °C for 3 h (5% H₂ and 95% N₂) before use. The catalysts were designated as Pd-mReO_x/C, in which m referred to the nominal weight loading of Re in this catalyst. The weight percentage of Pd in all the catalysts was fixed at 3 wt%.

2.3. Catalyst characterization

The nanoparticle size distribution of the metal particles was measured by Tecnai G2 F20 S-TWIN transmission electron microscope operated at 200 kV. X-ray powder diffraction (XRD) patterns were acquired on a Bruker D8 advance X-ray diffraction meter under Cu-Kα radiation. Metal leaching after reaction was measured by Thermo IRIS Intrepid II XSP atomic emission spectrometer. Nitrogen adsorption-desorption experiments were carried out on a Micromeritics ASAP 2020 static volumetric sorption analyzer. Temperature-programmed reduction in hydrogen (H₂-TPR) and temperature-programmed desorption of ammonia (NH₃-TPD) were conducted using a Micromeritics Autochem 2920 chemisorption analyzer. As for the H₂-TPR analysis, in a typical procedure, 0.1 g unreduced catalyst was placed in a quartz U-tube and degassed at 150 °C for 2 h. The sample was then cooled to 50 °C and reduced under hydrogen flow at the rate of 10 °C/min. For the NH₃-TPD analysis, 0.1 g catalyst was first placed in a quartz U-tube and then degassed at 150 °C for 2 h. The sample was then cooled to 100 °C to absorb ammonia for 2 h. The desorption procedure was performed at the heating rate of 10 °C/min to 800 °C.

2.4. Catalytic reaction

IA hydrogenation reactions were conducted in a 50 mL stainless steel autoclave with magnetic stirring. In every experiment, 0.2 g IA, 0.1 g catalyst and 20 mL deionized water were placed in the autoclave. Afterwards, the autoclave was purged with hydrogen for five times to remove air and pressured up to the desired hydrogen pressure and then heated to the reaction temperature.

Qualitative analysis of the reaction products was performed on a gas chromatography (GC, Shimadzu, 2010 plus) coupled with a mass spectrometer (MS, Shimadzu, QP 2010 Ultra) using an Rtx@-Wax column (30 m × 0.25 mm; film thickness, 0.25 μm). The reaction product was analyzed by both high performance liquid chromatography (HPLC) and GC. HPLC (Waters 1525) equipped with UV and evaporative light scattering (ELS) detectors was

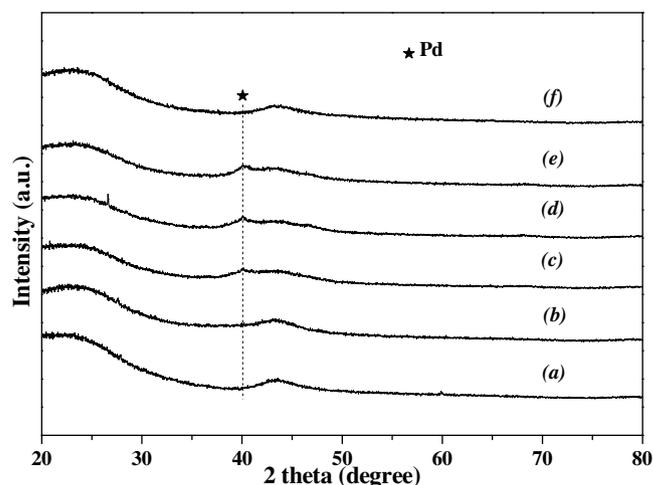


Fig. 1. XRD patterns of Pd-ReO_x/C with different Re content. (a) Active carbon, (b) Pd/C, (c) Pd-0.5ReO_x/C, (d) Pd-1ReO_x/C, (e) Pd-3ReO_x/C and (f) 3ReO_x/C.

used to quantify the residual reactant. An Aminex HPX-87H column (300 mm × 7.8 mm) eluted with 5 mmol/L H₂SO₄ solution (0.5 mL/min) was used at 35 °C to separate the reactant and products. GC (Shimadzu, 2010 plus) equipped with an FID detector using an Rtx@-Wax column (30 m × 0.25 mm; film thickness, 0.25 μm) was employed to quantify the products. Temperatures of the injector and detector were selected at 250 °C and 280 °C, respectively.

Conversion of IA was calculated by the Formula (1). For the complete conversion of IA could be obtained within very short reaction time, [17] it is hard to distinguish the differences in catalytic performance over different catalysts. Therefore, the conversion based on the methyl-succinic acid (MSA) should be better to clarify the catalyst activity. In this reaction, n_{IA}^{in} was equal to n_{MSA}^{in} . Conversion based on MSA was calculated by Formula (2). Selectivity of the product was calculated by the Formulas (3) and (4).

$$IA \text{ conversion (\%)} = \frac{n_{IA}^{in} - n_{IA}^{det}}{n_{IA}^{in}} \times 100 \quad (1)$$

$$MSA \text{ conversion (\%)} = \frac{n_{IA}^{in} - n_{MSA}^{det}}{n_{IA}^{in}} \times 100 \quad (2)$$

$$MGBL \text{ Selectivity (\%)} = \frac{n_{MGBL}^{det}}{n_{IA}^{in} - n_{IA}^{det}} \times 100 \quad (3)$$

$$MBDO \text{ Selectivity (\%)} = \frac{n_{MBDO}^{det}}{n_{IA}^{in} - n_{IA}^{det}} \times 100 \quad (4)$$

Where “ n^{in} ” means the initial amount of reactant, “ n^{det} ” means the amount of the reactant or products detected after reaction.

3. Results and discussion

3.1. Catalysts characterization

Fig. 1 shows the XRD patterns of Pd-ReO_x/C catalysts with active carbon as the reference. No obvious changes could be observed between active carbon and Pd/C catalysts, whereas a diffraction peak belonging to Pd (111) emerged as the Re content increased to 0.5 wt%, 1 wt% and 3 wt%, showing the increase tendency of Pd metal particles as the addition of Re. These results were further confirmed by the TEM images of Pd-ReO_x/C catalysts. Fig. 2 shows the TEM images of Pd-ReO_x/C catalysts. Pd nanoparticles were small-sized and well dispersed on the carbon support in the Pd/C catalyst, which was similar to the XRD analysis. Mean size of the metal

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