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Hydrogenation of methyl methacrylate under mild conditions using biosynthesis Ru catalyst

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ABSTRACT

Hydrogenation of methyl methacrylate (MMA) was investigated over Ru-based catalyst supported on active carbons (AC), which was prepared by bio-reduction method, using C. Platycladi (CP) leaf extract as reductant. By varying reaction temperature, hydrogen pressure and reaction time, hydrogenation of MMA over the biosynthesis Ru-based catalyst was carried out, and resulted the optimum conditions, 30 °C (room temperature), 2.0 MPa, and 50 min. The as-prepared Ru/AC catalyst showed high catalytic activity towards the hydrogenation of MMA, affording 100% of MMA conversion even under mild conditions without solvent and methyl isobutyrate was the only product.

Introduction

As an important intermediate materials, methyl methacrylate (MMA) has been used in a great amount to produce various types of polymers, such as plexiglass (PMMA) [1,2], MMA–styrene–butadiene copolymer, resins, coatings, adhesive agents, etc. [3]. With the expansion of MMA production capacity and the surplus of PMMA, new MMA applications should be brought up and a feasible one is to produce isobutyric acid (AIB) by MMA hydrogenation. AIB is the initial material to synthesize 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO), and CBDO is an important monomer for Tritan^{TM} copolyester, which is produced by Eastman Chemical Company. With various excellent properties, such as glass transition temperature, impact strength, weather ability and hydrolytic stability [4–6], this novel copolyester could substitute for polycarbonate polymer (PC) in medical devices, container and packaging [7]. Then a new synthesis flow of CBDO from MMA was summarized in Scheme 1. Methyl isobutyrate was successfully synthesized by the hydrogenation of MMA over the Ru/C, which can be easily hydrolyzed to AIB. Feed AIB to a pyrolysis zone produce a vapor effluent comprising dimethyl ketone (DMK) and then cool the vapor effluent to condense AIB and separate the condense from the DMK vapor. Followed by, the DMK vapor was added to an absorption zone wherein the DMK vapor produced an effluent comprising a solution of DMK in the solvent, and the effluent is heated to convert DMK to 2,2,4,4-tetramethylcyclobutane-1,3-dione (TMCB) in a dimerization zone. Finally, the TMCB was contacted with hydrogen in the presence of a catalyst comprising Ru to form a CBDO [8,9].

The hydrogenation of MMA was rarely involved in the previous publications. For the hydrogenation of unsaturated eaters, Aldea et al. [10] had reported a montmorillonite supported Ru-clays catalyst, and the yield of methyl isobutyrate could reach 85–91% at 75 °C and 4 MPa, with 100% conversion of MMA and long reaction time 45 h. Over supported palladium on magnetic nanoparticles, the hydrogenation of olefin was studied by Kim and Kim [11]. When it came to MMA, the yield of methyl isobutyrate was 97% with methanol solvent, under 1 atm of H_2 at room temperature. But more complicated separation and purification process should be involved for methanol solvent. Similarly, Natour and Abu-Reziq [12] used palladium based catalyst on magnetically separable polyurea nanosupport which was efficient in selectively hydrogenation reaction of α,β-unsaturated compounds. They reported MMA conversion of 100% at 50 °C in 2 h. Therefore, moderate reaction condition was the big superiority for the hydrogenation of MMA. Recently, some mild conditions under supercritical carbon dioxide have reported [13], involving complicated supercritical carbon dioxide system, lead to difficulty in industrial implement. In this paper, a new biosynthesis Ru catalyst was prepared and used to catalyze the hydrogenation reaction of MMA, which was easy to go under mild condition (room temperature, 2 MPa) and methyl isobutyrate was the only product.

The chemoselectivity toward two or more reducible functional group in the catalytic hydrogenation is of great importance.

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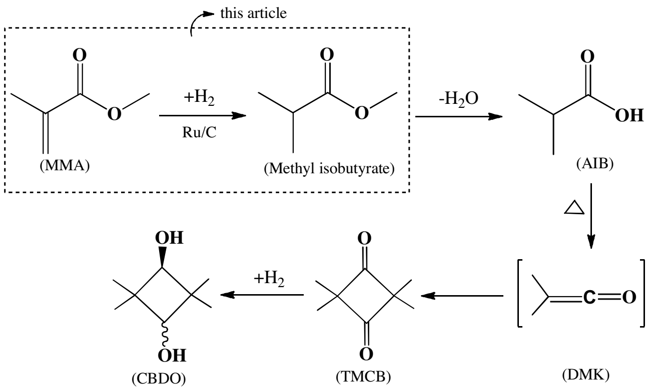

Scheme 1. The synthesis scheme of CBDO from MMA.

Selective, and particularly chemoselective, catalytic hydrogenation of α,β-unsaturated organic compounds is an essential and desirable process in synthetic chemistry and chemical industries [12,14,15]. Yabe et al. [16] developed heterogeneous palladium catalysts which enabled the chemoselective hydrogenation of azide, alkene and alkyne in the presence of other reducible functionalities. In Wienhofer et al.'s [7] research, a selective iron-based catalyst for the hydrogenation of α,β-unsaturated aldehydes to allylic alcohols was presented and successfully achieved the excellent chemoselectivity for the reduction of aldehydes in the presence of other reducible moieties. In this study, an efficient catalyst based ruthenium [17] made by eco-friendly plant reduction strategy [18] was used in this hydrogenation system and could successfully be selective for the hydrogenation of C=C bonds [19] while keeping the carbonyl group intact.

Noble metal catalysts on active carbon have showed great advantages to many selectively hydrogenations and different metal plays critical role. Bogel-Łukasik et al. [20] used Pt- and Pd-catalysts on limonene hydrogenation, observed that palladium as catalyst promotes regioselectivity and *trans* and *cis*-*p*-menthane are formed in 2:1 ratio, whereas the platinum catalyst produces them in 1:1 ratio. Upare et al. [15] researched the hydrogenation of levulinic acid over Ru/C, Pt/C, and Pd/C, and Ru/C was found to be the most active and product selective toward γ-valerolactone. We have previously investigated the Ru/C catalysts for the selective hydrogenation of maleic anhydride. In fact, the active carbon supported Ru nanoparticles could exhibit both desirable activity and stability for 99.2% yield of succinic anhydride without further hydrogenation to γ-valerolactone [4].

As was reported in the previous works [4,21–23], the biosynthesis of the Ru nanoparticles on the nanoscale materials carbon support is successfully prepared. Hence, the aim of this work is to apply the bioreduction Ru/AC catalysts to boost the liquid hydrogenation [24] of MMA to methyl isobutyrate under mild condition. Furthermore, in order to optimize the hydrogenation process, the influences of various reaction conditions on the catalytic performance were also studied. Several analysis techniques, such as low temperature N_2 physisorption, X-ray diffraction (XRD), transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) were adopted to offer insights of the intrinsic structure property relationship of the catalysts.

Experimental

Materials

Carbon (Activated charcoal, LOT-242276) was purchased from Sigma–Aldrich, C. Platycladi (CP) leaf was obtained from Zhejiang university hospital. Methyl methacrylate (AR, >99%) was purchased from Aladdin Chemical Co., Ltd. Other chemical reagents mentioned were analytic grade from Sinopharm Chemical Reagent Co., Ltd. and used directly without pretreatment. The deionized water was used in all synthesis and washing processes of the whole experiment.

Catalyst preparation

The Ru-based catalyst was prepared by the adsorption–bioreduction method using the as-prepared CP extract which was reported in detail in previous papers [4]. 0.6 g AC was weighed in a 100 mL conical flask and then impregnated with an aqueous $RuCl_3$ solution (50 mL, 2.3 mmol/L). The system was placed in an oil bath(60 °C) with the proper stir for 1 h. Then 30 mL CP extract were slowly added to the solution and continually stirred for another 5 h. After that, the suspension was filtered, washed with water until the neutral pH and dried overnight at 60 °C in vacuum. Finally, the dried catalyst was calcined under H_2 at 400 °C for 3 h. The loading amount of the Ru metal were all 2.0 wt%.

Catalysts characterization

The Micromeritics ASAP 2020 instrument was applied for monitoring the low-temperature N_2 adsorption–desorption behaviors to get the Brunauer–Emmet–Teller (BET) specific surface areas and the total pore volume and pore size counted by Barrett–Joyner–Halenda (BJH) method. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) with energy dispersive X-ray spectroscopy (EDX) images were measured with a FEI Tecnai G2 F20 S-TWIN microscope operated at an accelerating voltage of 200 kV. The specimens were prepared by ultrasonically suspending the small amount of powder sample in ethanol for 30 min and dropped on the copper grids with carbon support films. XPS experiments were performed on a VG ESCALAB MARK II equipment with monochromatic radiation of Mg $K\alpha$ (BE = 1253.6 eV). XRD patterns were collected on Shimadzu powder X-ray diffractometer with Cu $K\alpha$ radiation (= 0.154 nm) at 40 kV and 30 mA using the scanning angle 2θ ranging from 10° to 90°, at a step of 0.02°/s and rate of 2°/min.

Catalyst evaluation

The hydrogenation of MMA to methyl isobutyrate was carried out in a 100 mL stainless steel high pressure batch-type reactor equipped with magnetic stirrer. In a typical experiment, 10 mL MMA and 0.15 g the biosynthesis Ru-based catalyst were charged into the reactor. The reactor was then sealed and purged with flowing N_2 and H_2 at 4–6 MPa twice respectively in the absence of stirring to replace the air. Sequentially, charged with H_2 at setting pressure at room temperature and then heated to working temperature. The pressure and temperature change with time were recorded to observe the reaction parameter variation. After the planning reaction time, the reactor was speedily cooled down to room temperature in water bath within 5 min and depressurized the remaining pressure. The reaction product discharged from reactor was separated for further analysis by gas chromatograph (Kexiao, GC-1690) equipped with OV-1 capillary column and a FID.

The MMA conversion which was defined as the ratio of reacted MMA to initial MMA and turnover frequency (TOF) were calculated and used to evaluate the catalytic performance. The TOF value was defined as the number of MMA that converted per hour per total amount of Ru site used in the catalyst. Besides, the recyclability of the catalyst was also studied. After the hydrogenation, the used catalyst was collected and separated from the product by vacuum filtration. The catalyst was washed by ethanol and water for

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