

Oxidation of aromatic oxygenates for the production of terephthalic acid

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ARTICLE INFO

Keywords:

Terephthalic acid
Oxidation
Iridium
Free radical

ABSTRACT

We study the production of terephthalic acid (TA) from biomass-derived aromatic oxygenates. Among several heterogeneous catalysts tested, a carbon-supported Ir catalyst in 4-heptanone solvent gives the best TA yield from 1,4-dihydroxymethylbenzene. A maximum 76% TA yield is achieved at 100 °C and 12 bar O₂. Based on kinetic measurements, we show that the reaction progresses in two distinct pathways. First, the alcohol groups of the substrate are converted to the aldehydes via an O-assisted dehydrogenation pathway over Ir, and then the aldehydes are oxidized to the acid in the solution via a free radical mechanism. We demonstrate that it is easier to oxidize aromatic diols than p-xylene over a heterogeneous catalyst, and thus, the biomass route to TA may be an attractive alternative to the commercial crude oil-based process.

1. Introduction

Terephthalic acid (TA), an important commodity chemical with global annual production of more than 50 million tons (2014) and an average annual market growth of > 5% [1], is largely used for polyethylene terephthalate (PET) production, which is then converted to thousands of household consumable goods including fibers and packing materials [1].

Currently, TA is produced via aerobic oxidation of petroleum-derived p-xylene (pX) with O₂ using a homogeneous catalyst, comprising of cobalt acetate, manganese acetate and bromide ions, in acetic acid solvent [2]. In addition to the Mn(II) cocatalyst [3,4], promoters such as organic [5] and inorganic [3] bromides, and miscellaneous inorganic salts [6,7] are extensively used to facilitate the redox cycling of Co between the +2 and +3 oxidation states [7]. Despite this process being commercial, it is highly corrosive and forms ozone-depleting methyl bromide. Thus, the process requires careful design using expensive materials [8] and poses sustainability challenges, as the current source of pX is petroleum.

Heterogeneous catalysis has been used for pX oxidation to overcome the challenges associated with homogeneous catalysis. Chavan et al. reported the encapsulation of Co and Mn complexes into a zeolite and achieved yields greater than 98% for the oxidation of pX to TA. However, this system requires acetic acid as a solvent and Br⁻ as a promoter [9]. Deori et al. used CeO₂ nanoparticles to catalyze the oxidation of pX in water, reporting excellent TA yields under mild

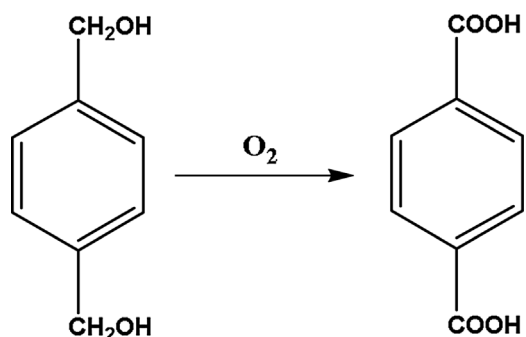
conditions (70 °C, 1 bar O₂) [10,11].

To address the sustainability challenges posed by the use of petroleum-derived pX, the production of renewable TA from biomass has been extensively researched [12]. It has recently been demonstrated that pX can be produced via the hydrodeoxygenation of 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF) [13,14] followed by Diels-Alder reaction of DMF with ethylene [15,16]. This approach can afford pX with high yield [17]. Other researchers have reported the synthesis of 4-methylbenzoic acid (p-toluic acid) via Diels-Alder reaction of isoprene and acrylic acid, followed by dehydrogenation [18,19]. A similar approach was reported by Weckhuysen and coworkers, in which o- and m-toluic acids were produced from furan and maleic anhydride [20,21]. All of the aforementioned methods require multiple steps (reduction, condensation) to produce TA precursors that can be finally oxidized. Alternative methods to eliminate the reduction step have recently been proposed by Pacheco and Davis [22–24], in which partially oxidized HMF derivatives undergo Diels-Alder condensation over Lewis acidic zeolites (e.g., Zr-BEA). This methodology afforded p-methoxymethyl-benzoic acid with 81% selectivity at 26% conversion [22]. Based on these initial encouraging results, further work may improve the yield of oxygenated diatomics.

To date, there has been little work on the final oxidation step to convert oxygenated Diels-Alder products to TA. It is therefore important to assess if a heterogeneous catalyst-based process of converting lignocellulosic biomass to TA is feasible without the intermediate hydrodeoxygenation of furanic molecules to (DMF). We used DHMB as a

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Scheme 1. Oxidation of di-(hydroxymethyl) benzene (DHMB) to TA.

model aromatic oxygenate to produce TA (Scheme 1) over heterogeneous catalysts and systematically optimized the oxidation conditions, achieving a maximum TA yield of 76%. While DHMB is currently more expensive than TA, because it is produced by reduction of TA or dimethyl terephthalate with LiAlH_4 , optimization of Diels-Alder processes for the production of DHMB and related molecules, may render the entire process economically viable. Kinetic measurements elucidate the reaction network and demonstrate the relevance of the system for understanding the oxidation of all intermediate oxygenates. We show that while alcohols undergo dehydrogenation over the metal catalyst, the oxidation of the resulting aldehydes to acids proceeds homogeneously in solution via a radical mechanism. Given the difficulty in oxidizing the *p*-xylene in the traditional process, our work addresses another important question, namely if there is any benefit by having oxidized side groups in the selective oxidation to TA.

2. Materials and methods

2.1. Materials and reagents

The metal catalysts were obtained from Sigma Aldrich (10% Pt/C, 10% Pd/C, 3% Cu/C, 5% Rh/C, and 5% Ru/C) and Premetek (10% Ir/C and 20% Au/C). Carbon black (VXC-72) was obtained from Cabot. 1,4-di-hydroxymethylbenzene (DHMB-99%) was obtained from Tokyo Chemical Industry. Terephthalaldehyde (TALD-99%), 4-formylbenzoic acid (FBA-97%), terephthalic acid (TA-98%) were obtained from Sigma Aldrich. 4-hydroxymethylbenzoic acid (HMBAC-98%) was obtained from Alfa Aesar. 4-(hydroxymethyl)benzaldehyde (HMBA-98%) was purchased from Ark Pharm. 4-heptanone (98%) and *N,O*-bis-trimethylsilylacetamide (BSA, 95%) were purchased from Acros Organics, toluene (99.9%) and diglyme (99%) were purchased from Fisher Scientific. 1-octanol (99%), *N*-methyl-2-pyrrolidone (99.5%, NMP) and tert-butanol (99%) were purchased from Sigma-Aldrich. All reagents were used without further purification.

2.2. Catalysis and products analysis

In a typical reaction, the catalyst (10:1 Ir:DHMB ratio) was placed in a Q-tube (QLabtech) with 50 mg of DHMB, 1 mL of solvent, and a stir bar. Unless otherwise noted, the solvent used was 4-heptanone. The tube was sealed with a septum and the system was subsequently evacuated using the building vacuum system. Then, a syringe filled with O_2 (4.4 purity grade, Keen gas) was inserted through the septum (Fig. S1) and the tube placed in a pre-heated aluminum block situated on a stirring plate. For the catalyst screening experiments, we varied the reaction time to achieve 60–75% conversion. When the reaction was too fast and achieved full conversion in less than 1 h, we reduced the catalyst amount to achieve the required conversion. Similarly, when the reaction was too slow, we increased the catalyst amount to achieve the required conversion in less than 20 h. For the high-pressure experiments, we used the gas purging system for Qtubes (QLabtech) to

pressurize and hold the system at the desired pressure. The maximum rated pressure of the septa is 12 bar, while the tubes are rated to 33 bar.

After the reaction, the tubes were cooled down and the pressure (if the system was pressurized) was released. Then, a known mass of 1-octanol as an internal standard was added to the reaction product mixture, which was reacted with 2 mL of BSA, in order to silylate the acids and alcohols in the reaction mixture. This was done to ensure good chromatographic characteristics of these compounds. 7 mL of acetone were added into the tube and the mixture was heated to its boiling point (60 °C) for 10 min to ensure complete silylation of the acids and alcohols in the mixture. An aliquot was then analyzed using an Agilent 7890A gas chromatograph, equipped with an HP-1 capillary column (30 m × 0.32 mm × 0.25 μm - Agilent) and a flame ionization detector (FID). Detailed GC and GC/MS operating conditions can be found in the supporting information (Table S1). The response factors of all reactants, intermediates, and products were calculated using mixtures of standard compounds with known concentrations. Unknown products were identified using a GC/MS (Agilent 7890B – 5977 MS), equipped with an HP-5 column (30 m × 0.25 mm × 0.25 μm) and the NIST 2016 spectral library.

2.3. Instrumentation

X-ray photoelectron spectroscopy (XPS) of the fresh and spent catalysts was performed at the Surface Analysis Facility of the University of Delaware. A Thermo Scientific KAlpha + instrument equipped with an Al Ka source was used. Powdered samples were spread on carbon tape prior to analysis and a spot size of 400 μm was used. An electron flood gun was used to prevent charging of the sample.

Particle size distributions of supported metal catalysts were determined using transmission electron microscopy (TEM). TEM analysis was performed at the Keck Center for Advanced microscopy at the University of Delaware. A JEOL JEM-3010 electron microscope was used at 300 kV tension. Below, the surface average diameter is reported.

3. Results and discussion

First, we screened several carbon-supported catalysts. Initial experiments were conducted for 20 h (Fig. S2). Negligible conversion of DHMB to products is observed with carbon black (Vulcan XC72) and in the absence of catalyst. The Pd catalyst leads to high conversion of DHMB but low yields of oxidation products. Prior studies have demonstrated that C–C bond scission of aldehydes over Pd is quite facile [25,26], which is consistent with the detection of benzoic acid in the products. A similar trend is observed for Pt, which has also been reported as a good catalyst for C–C bond scission reactions [27]. Oxidation over a Ru catalyst yields mostly TALD [28,29]. Other catalysts, such as Au [30–33] and Cu [34], only catalyze the oxidation to yield HMBA as the major product. Ir/C [35] performs the best, yielding 93% oxidation products including 55% TA at complete conversion of DHMB.

Comparison of the intrinsic selectivity of the catalysts at similar conversion of 60–75%, at appropriate reaction times, is shown in Fig. 1. The Ir catalyst gives minimal loss of carbon, achieving 51% HMBA and 13% TALD yields at 65% DHMB conversion. Flaherty et al. have reported ring-opening [36] and other C–C bond scission reactions [37] over Ir under high H_2 pressure (up to 40 bar) in which the ring-opening of toluene occurred via partial ring hydrogenation [36]. The presence of O_2 in our reaction could prevent these side reactions and drive the thermodynamic equilibrium to the products. Given the lower carbon loss over Ir/C, this catalyst has been selected for further studies.

Higher oxygen pressure (from 1 bar to 5 bar at 90 °C) improves TA yield to 71% after 20 h of reaction (Fig. S3). At shorter reaction time (2 h), selectivity shifts from HMBA to TALD as the O_2 pressure increases from 1 bar to 5 bar but further increase in O_2 pressure does not significantly affect selectivity (Fig. 2).

Fig. 3 shows that the conversion of the substrate and the yield of TA

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