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Low-temperature oxidation of guaiacol to maleic acid over TS-1 catalyst in alkaline aqueous H_2O_2 solutions

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ABSTRACT

To mitigate the negative environmental impact of greenhouse gas (GHG) emission originated from the use of fossil fuels, the chemical world is switching to utilize renewable biomass resources. Co-producing value-added chemicals is important for an integrated biorefinery to improve economics of biofuels. Lignin derived compounds, e.g. guaiacol, are common by-products of fast pyrolysis of lignocellulosic biomass. In this paper, the feasibility of low-temperature selective oxidation of guaiacol to value-added dicarboxylic acids, e.g. maleic acid, was investigated using titanium silicalite/hydrogen peroxide (TS-1/H_2O_2) reaction system. Under the reaction conditions (80 °C and the initial pH = 13.3), the molar yields of maleic acid from guaiacol were approximately 20%–30%. The effects of catalyst amount, initial pH values, reaction time, and temperature on the yields of maleic acid were investigated. A possible reaction mechanism of TS-1 catalyzed aromatic ring opening was proposed.

1. Introduction

Lignocellulosic biomass is an abundant renewable feedstock resource for biorefineries to produce fuels and chemicals [1]. In biorefinery industry, fast pyrolysis is a thermochemical process which can produce up to 70 wt% bio-oils from raw biomass and is being deployed at pilot-scale [2–8]. However, due to the high oxygen contents (35–40 wt%), low heating values, instability, corrosiveness, and immiscibility with gasoline and diesel, the bio-oil products cannot be used as liquid transportation fuels without substantial upgrading [9,10]. Hydrodeoxygenation (HDO) is extensively studied for upgrading pyrolysis oil [11–13]. However, the H_2 consumption for upgrading pyrolysis oil is a major hurdle of making HDO cost-effective. Especially, due to the unselective nature of HDO, unnecessary saturation of aromatic molecules, which account for ~30 wt% of the total pyrolysis oil, causes excess H_2 consumption and therefore makes HDO cost-prohibitive, considering the low profit margin of fuel products [14]. In contrast, selective oxidation of low-value lignin derived compounds into value-added commodity chemicals could improve the overall process economics of a biorefinery.

Guaiacol (2-methoxyphenol), one of the major lignin-derived bio-oil components, is widely used as the model feed for HDO upgrading [15–31]. However, the catalytic upgrading of guaiacol via oxidation methods is much less explored. Sasaki's group reported that the main products of hydrothermal oxidation of guaiacol in sub- and super- critical water were catechol, phenol, and *o*-cresol [32,33]. Suzuki et al. [34] found that guaiacol was unselectively oxidized to low-molecular weight carboxylic acids like acetic acid and formic acid with molecular oxygen in aqueous media at 300 °C. Although the mechanistic

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studies of guaiacol oxidation were scarce in literature, knowledge learned from extensive studies of mineralization of phenol, a common water pollutant, by catalytic wet oxidation can be leveraged since phenol is a possible intermediate during guaiacol oxidation. The main intermediate products detected in phenol mineralization were ring compounds (hydroquinone, catechol, benzoquinones, etc.), and short chain carboxylic acids including maleic, malonic, succinic, fumaric, formic, acetic, and oxalic acids. However the yields of organic acids, especially C_4 diacids, were negligible [35–40].

Among the biomass-derived dicarboxylic acids, maleic acid is an important raw material used in the manufacture of phthalic-type alkyd and unsaturated polyester resins, surface coatings, lubricant additives, plasticizers, copolymers, and so on [41]. Industrial processes of the production of maleic anhydride, a dehydrated form of maleic acid, use petroleum-based butane or benzene as the feedstock. Thus oxidation of lignin derived by-products would be an appealing process to produce green maleic acid. The challenge, however, is how to cost-effectively accomplish a high yield of the desired carboxylic acid product.

Our group recently found that levulinic acid was generated in a high production yield by the aqueous-phase partial oxidation of cellulose over the ZrO_2 catalyst via a possible radical reaction pathway [42]. Herein, we expand our searching for heterogeneous oxidation catalysts for the selective conversion of lignin-derived compounds. Titanium silicalite-1 (TS-1), a synthetic zeolite in which a small number of Ti atoms substitute tetrahedral Si atoms in a purely siliceous framework with the MFI structure[43], is an active and selective catalyst for a number of low-temperature oxidation reactions with aqueous H_2O_2 as the oxidant. The TS-1/H_2O_2 reaction system has been one of the most actively studied green processes in the past decade [44–46]. In the present study, we demonstrate the feasibility of the selective oxidation of guaiacol to produce maleic acid with TS-1/H_2O_2 under mild conditions. In addition, the oxidative ring-opening reaction mechanism is also tentatively discussed.

2. Experimental

2.1. Catalyst preparation and characterization

The TS-1 catalyst (Si/Ti ratio is 33) was synthesized using the modified method in literature [43]. Briefly, 50 g tetraethyl orthosilicate (TEOS) was added into 70 g aqueous solution of 20 wt% tetrapropylammonium hydroxide (TPAOH). To the resultant clear solution, a solution of 2.3 g titanium butoxide ($Ti(OBu)_4$) in isopropyl alcohol (15 g) was added and then 60 g water was added. The mixture was crystallized at 160 °C for 12 h under autogeneous pressure. The as-synthesized samples were calcined at 540 °C for 5 h before use. All TS-1 precursors were bought from Sigma Aldrich. Other materials including Al_2O_3, and H-ZSM-5 were purchased from Alfa Aesar. The surface morphology of catalysts was characterized by a Hitachi S-4700 scanning electron microscopy (SEM). Raman spectra were obtained on Renishaw InVia Raman Microscope System with the excitation laser wavelength of 512 nm. Electron paramagnetic resonance (EPR) spectra were recorded at room temperature in air using a Bruker EMX Plus spectrometer operated in the X band with 100-kHz field modulation with 10 mW microwave power, 100 kHz modulation frequency, 1G modulation amplitude, 30 dB receiver gain, 0.01 ms time constant, 100 G scan range, 35 s scan time, and 8 number of scan.

2.2. Aqueous-phase oxidation

The aqueous-phase oxidation reaction experiments were carried out in the leak-proof 30mL perfluoroalkoxy (PFA) vials (Thermo Scientific). In a typical experiment, 10 mL of aqueous solution of guaiacol (10 wt%), 0.5 mL H_2O_2 solution (35 wt%) and 0.1g solid catalyst were added into each PFA vial. Eight vials were fixed on the rotating vial holder and then placed in a preheated oven at the set temperature. The rotational speed was at 90 r/min to ensure a good mixing of catalysts in aqueous solutions. The schematic diagram of the reactor is shown in Fig. 1. After the reaction, the vials were quenched immediately in an ice water bath.

2.3. Product analysis

Aqueous samples collected from the oxidation experiments were diluted as needed and filtered through a 0.22-μm pore-size filter for analysis using total organic carbon (TOC) analyzer, high performance liquid chromatography (HPLC), electrospray ionization mass spectrometer (ESI-MS), and gas chromatography with mass spectrometer detector (GC/MS). TOC was measured by a Shimadzu Total Organic Carbon Analyzer (model TOC-V). HPLC analysis was performed using a Shimadzu HPLC system equipped with a dual UV-VIS Detector (Shimadzu SPD 10-AV) at 208 and 290 nm and a Refractive Index Detector (Shimadzu RID-10A). For the analysis of organic acids and reaction intermediates, the samples were separated in an Aminex 87-H column from Bio-Rad, with 5 mmol/L H_2SO_4 as the mobile phase (0.7 mL/min) and a column temperature of 55 °C. All samples for ESI-MS analysis were diluted with a base solution containing 0.1 wt% triethylamine and the analysis was performed using a Waters Micromass ZQ quadrupole mass spectrometer. GC/MS analysis was carried out using an Agilent

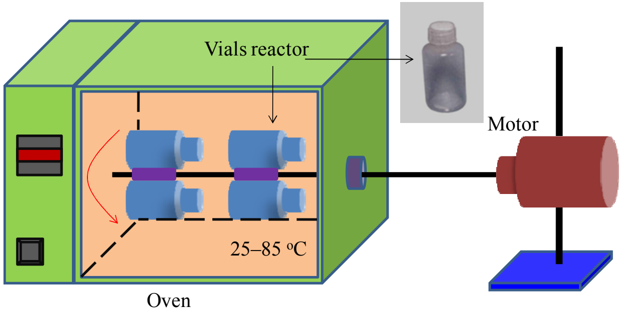

Fig. 1. Schematic diagram of the aqueous-phase oxidation reactor system. Eight leak-proof 30 ml narrow-mouth PFA vials were placed in the bottle holder, which was rotated at 90 r/min along the horizontal axis driven by an external motor. The reaction temperature was controlled by a preheated oven.