Production of Benzoic Acid from Biomass-Derived Furan and Methyl Acrylate Using Lewis Acidic Zeolites

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Introduction

Benzoic acid is a commodity chemical that can be used to produce monomers for phenolic resin, epoxy resin, polycarbonate, and Nylon 6 synthesis. Benzoic acid is also used as precursor to small-molecule drugs, as food and industrial preservative, for plasticizers, and many other applications. It is produced at a 130,000 mt/year capacity in North America [1] from fossil fuels but it can be potentially produced from renewable carbon sources.

We have used a selective two step-reaction sequence to convert furan—a hemicellulose derived species [2]—into benzoic acid in high yield and high selectivity (Scheme 1). In this report we show that Lewis-acid containing zeolite beta quantitatively catalyzes the Diels-Alder reaction of methyl acrylate and furan to oxanorbornene carboxylic methyl ester. This ester was dehydrated to produce methyl benzoate in 96% selectivity in binary mixtures of methanesulfonic acid (MSA) and acetic anhydride.

Scheme 1. Two step reaction sequence for the conversion of furan to methyl benzoate

Materials and Methods

Hafnium, zirconium, tin and siliceous zeolite beta were synthesized following reference [3] with minor modifications: instead of using hafnium chloride, hafnium oxychloride hydrate was added for gel synthesis. The zeolites were characterized by FTIR spectroscopy of adsorbed acetonitrile using a Mattson Galaxy FTIR with a diffuse-reflection attachment (Collector II). The Diels-Alder reaction was run by mixing 6.88 mmol of furan and 1.36 mmol of methyl acrylate or acrylic acid and 0.1 g of zeolite and reacting at 298 K for 24 hrs. The dehydration reaction was run at a 0.130 M concentration of oxanorbornene for 2 h at 298 K followed by a 1 h at 353 K. Yield and selectivity were determined using quantitative nuclear-magnetic resonance (qNMR) spectroscopy.

Results and Discussion

The uncatalyzed Diels-Alder reaction of furan and methyl acrylate is very slow [4] but it can be accelerated using Lewis acids. We have used microporous solid Lewis-acids (Hf-, Sn- and Zr-beta) to catalyze this reaction. FTIR spectra of deuterated acetonitrile adsorbed on siliceous- and HI- beta show that the spectrum of acetonitrile adsorbed on Hf-beta displays a new absorption peak 2303 cm$^{-1}$ indicative of a Lewis-acid base interaction. The FTIR spectra of acetonitrile adsorbed on Sn- and Zr-beta show similar features. Lewis-acid Hf-beta quantitatively catalyzes the Diels-Alder reaction to oxanorbornene carboxylic methyl ester, at a turnover rate of 3.7 h$^{-1}$ at 308 K at 23 hr. This turnover frequency is two-orders of magnitude higher than previously reported heterogeneous catalysts for this reaction [5]. Sn-beta and Zr-beta zeolites also catalyzed this reaction with high selectivity and comparable rates (Table 1).

The purified product, oxanorbornene carboxylic methyl ester, was then dehydrated to produce methyl benzoate in 96% selectivity using binary mixtures of MSA and acetic anhydride as the dehydrating agent. This selectivity was much higher than dehydration of the ester using neat MSA that produced methyl benzoate with only 1.7 % selectivity.

Table 1. Diels-Alder reaction of furan and acrylic acid catalyzed by Lewis-acidic zeolites

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>Turnover Frequency (h$^{-1}$) $^{[a]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf-Beta</td>
<td>51</td>
<td>5.08</td>
</tr>
<tr>
<td>Sn-Beta</td>
<td>31</td>
<td>5.00</td>
</tr>
<tr>
<td>Zr-Beta</td>
<td>48</td>
<td>4.54</td>
</tr>
<tr>
<td>Si-Beta</td>
<td>13</td>
<td>-</td>
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</tbody>
</table>

$^{[a]}$ Turnover frequency calculated by moles of oxanorbornene produced divided by moles of metal determined by ICP-OES

Significance

A two-step process for the preparation of benzoic acid from biomass-derived oxygenates (furan and methyl acrylate) has been demonstrated in high yield and high selectivity. Novel Lewis-acid containing microporous materials were shown to be effective catalysts for the Diels-Alder reaction. This process could be also be used to synthesize a number of commercially valuable aromatic species from biomass-derived precursors.

References