New Catalysts for the Renewable Production of Monomers for Bioplastics

Thesis by

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In Partial Fulfillment of the Requirements for

the Degree of Doctor of Philosophy

California Institute of Technology

Pasadena, CA

2015

(Defended May 12, 2015)

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ACKNOWLEDGMENTS

Many thanks and appreciation is given to my family for their never-ending love and support during my time as a Ph.D. student.

My fellow Ph.D. students and postdocs within the M.E. Davis group were indispensable during my graduate studies. It was truly a pleasure to have been able to work every day with some of the hardest working and brightest researchers in the field. Without the many great ideas that had arisen from discussions with them, this work would not have been possible.

To many others at Caltech, including Dr. Jay Labinger, Dr. Mona Shahgholi, Dr. Chi Ma, and Dr. David VanderVelde, I am greatly thankful for the advice and assistance that you offered me.

Lastly, I express my great appreciation to my advisor, Prof. Mark Davis, for bringing me into his research group and giving me the opportunity to join the exciting field of zeolite synthesis and catalysis.

ABSTRACT

Terephthalic acid (PTA) is one of the monomers used for the synthesis of the polyester, polyethylene terephthalate (PET), that is used for the large-scale manufacture of synthetic fibers and plastic bottles. PTA is largely produced from the liquid-phase oxidation of petroleum-derived p-xylene (PX). However, there are now ongoing worldwide efforts exploring alternative routes for producing PTA from renewable, biomass resources.

In this thesis, I present a new route to PTA starting from the biomass-derived platform chemical, 5-hydroxymethylfurfural (HMF). This route utilizes new, selective Diels-Alder-dehydration reactions involving ethylene and is advantageous over the previously proposed Diels-Alder-dehydration route to PTA from HMF via 2,5-dimethylfuran (DMF) since the H_2 reduction of HMF to DMF is avoided. Specifically, oxidized derivatives of HMF are reacted as is, or after etherification-esterification with methanol, with ethylene over solid Lewis acid catalysts that do not contain strong Brønsted acids in order to synthesize intermediates of PTA and its equally important diester, dimethyl terephthalate (DMT). The partially oxidized HMF, 5-(hydroxymethyl)furoic acid (HMFA) is reacted with high pressure ethylene over a pure-silica molecular sieve catalyst containing framework tin (Sn-Beta) to produce the Diels-Alder-dehydration product, 4-(hydroxymethyl)benzoic acid (HMBA), with ~30% selectivity at ~20% yield. If HMFA is protected with methanol to form methyl 5-(methoxymethyl)furan-2-carboxylate (MMFC), MMFC can react with ethylene in the presence of a pure-silica molecular sieve containing framework zirconium

(Zr-Beta) to produce methyl 4-(methoxymethyl)benzenecarboxylate (MMBC) with >70% selectivity at >20% yield. HMBA and MMBC can then be oxidized to produce PTA and DMT, respectively. When Lewis acid containing mesoporous silica (MCM-41) and amorphous silica, or Brønsted acid containing zeolites (Al-Beta), are used as catalysts, a significant decrease in selectivity/yield of the Diels-Alder-dehydration product is observed.

An investigation to elucidate the reaction network and side products in the conversion of MMFC to MMBC was performed, and the main side products are found to be methyl 4-formylcyclohexa-1,3-diene-1-carboxylate and the ethylene Diels-Alder adduct of this cyclohexadiene. These products presumably form by a different dehydration pathway of the MMFC/ethylene Diels-Alder adduct and should be included when determining the overall selectivity to PTA or DMT since, like MMBC, these compounds are precursors to PTA or DMT.

Fundamental physical and chemical information on the ethylene Diels-Alder-dehydration reactions catalyzed by the Lewis acid-containing molecular sieves was obtained. Madon-Boudart experiments using Zr-Beta as catalyst show that the reaction rates are limited by chemical kinetics only (physical transport limitations are not present), all the Zr^{4+} centers are incorporated into the framework of the molecular sieve, and the whole molecular sieve crystal is accessible for catalysis. Apparent activation energies using Zr-Beta are low, suggesting that the overall activation energy of the system may be determined by a collection of terms and is not the true activation energy of a single chemical step.

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