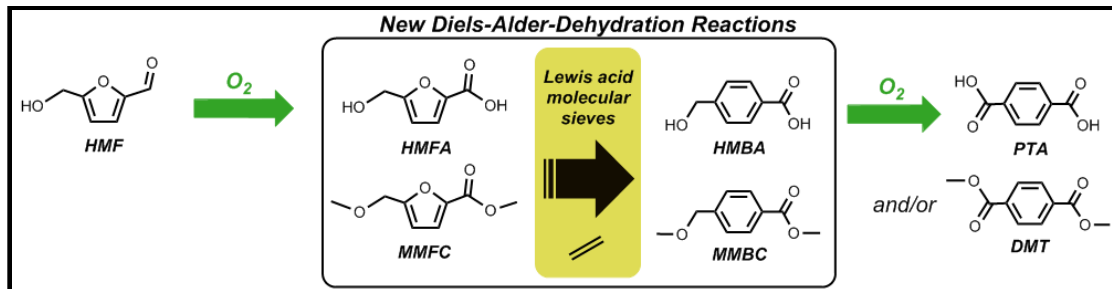


## CHAPTER 8

## CONCLUSION AND FUTURE RESEARCH

## 8.1 Conclusion

The motivation of this work was to develop new methods for the production of PTA for renewable PET polymers starting from biomass-derived HMF. New Diels-Alder reactions between oxidized variants of HMF and ethylene that are catalyzed by Lewis acid molecular sieves were discovered, and have opened a new pathway for the synthesis of PTA that does not require reduction steps (Fig. 8.1). The pathway allows for a novel method for the production of 100% renewable PET from biomass (Fig. 2).



**Fig. 8.1** New Diels-Alder-dehydration reactions possible using Lewis acid molecular sieves catalysts.

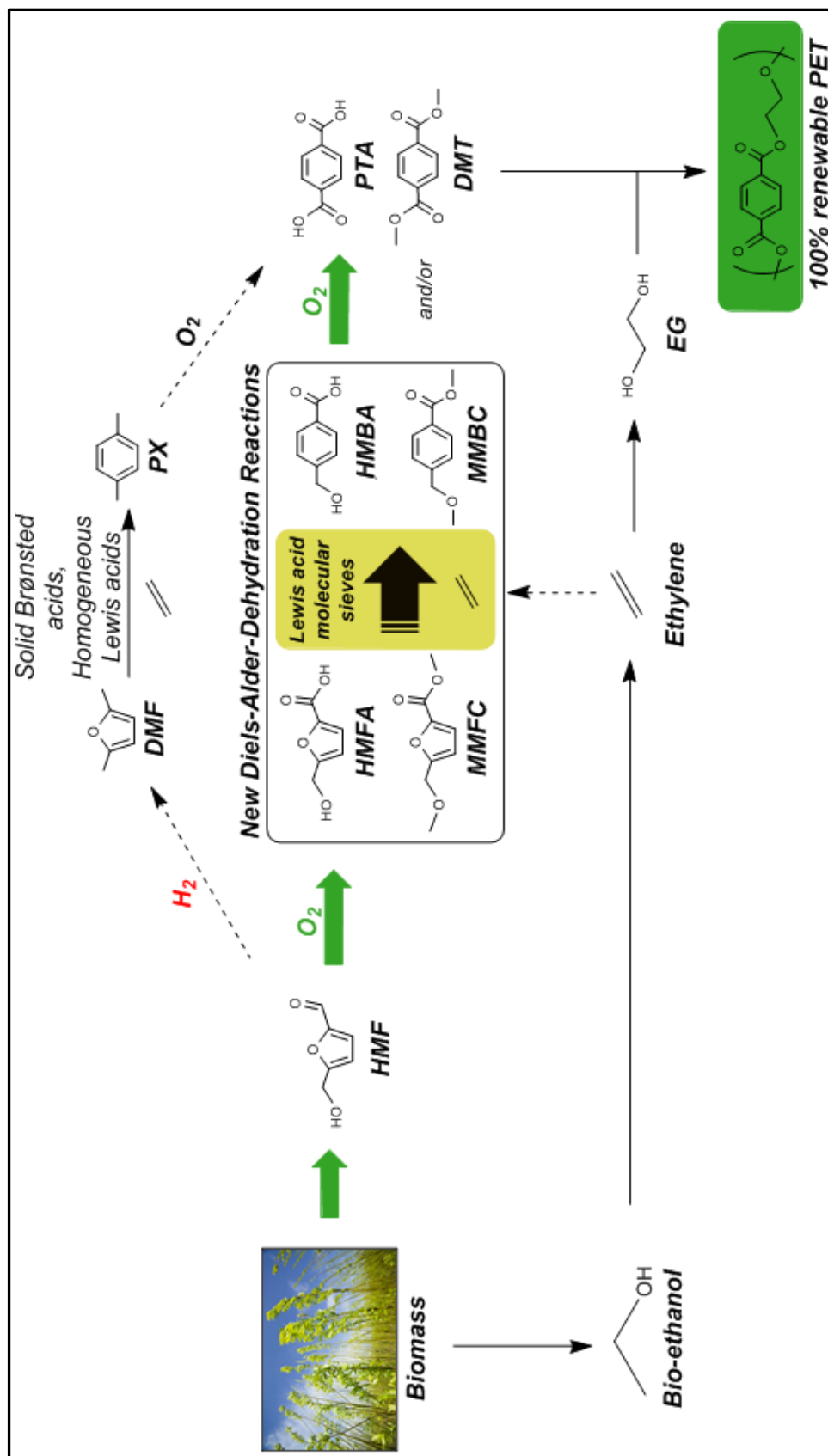


Fig. 8.2 New route to 100% renewable PET.

The work presented in this thesis has included synthesis of microporous materials for Lewis acid catalysis, exploratory research and development of new Diels-Alder-dehydration chemistry involving ethylene, and characterizations of the Diels-Alder-dehydration reaction systems that included side product identification and measurement of kinetic data (apparent activation energies).

Although there are numerous previous examples of Lewis acidic solid materials catalyzing Diels-Alder reactions, this is the first use of the series of pure silica molecular sieves containing Lewis acid metal centers in the zeolite framework (Sn-Beta, Zr-Beta, Ti-Beta) for catalyzing Diels-Alder reactions. The new Diels-Alder-dehydration reactions are unusual reactions involving furanic dienes with carboxylate group substituents that are known to usually deactivate the diene in Diels-Alder cycloadditions. These reactions are the first examples of oxygenated furans reacting at high temperatures and pressures with ethylene in Diels-Alder cycloadditions. The catalyst plays a key role in allowing the reactions to occur and an important characteristic of the catalyst is the lack of any strong Bronsted acidity since Bronsted acidity causes significant conversion and degradation of the oxygenated furans at the high temperature/pressure conditions required for ethylene to react. Confinement effects within the microporous environment of the Lewis acid molecular sieves may also be important for catalysis of some reactions since it was found that the Beta materials were the only effective catalysts for the reaction between MMFC and ethylene (the mesoporous and amorphous materials did not catalyze the reaction).

The elucidation of the key side products in the new Diels-Alder-dehydration reaction system involving MMFC and ethylene has resulted in the identification of novel cyclohexadiene-type compounds, that is methyl 4-formylcyclohexa-1,3-diene-1-carboxylate and methyl 4-formylbicyclo[2.2.2]oct-2-ene-1-carboxylate. These compounds may be considered PTA precursors and, therefore, are not necessarily undesired side products. These compounds may be included when calculating an overall selectivity to PTA precursors (MMBC, etc.) from HMF-derived MMFC.

The measurement of  $E_a$ 's for two different Diels-Alder-dehydration systems (DMF/PX, MMF/MPT) catalyzed by Zr-Beta reveal low apparent  $E_a$  values that are likely too low to be activation energies of a single chemical step. Instead, these data suggest the apparent  $E_a$ 's of the processes under the studied conditions may include a collection of terms that could result in low overall values. Since two reactions in tandem (Diels-Alder cycloaddition and dehydrative aromatization) occur over a heterogeneous surface, it is possible for the apparent  $E_a$ 's to be a combination of terms that may include the  $\Delta H_{rxn}$  for the reversible Diels-Alder reaction, the true  $E_a$  for the dehydrative aromatization of the Diels-Alder adduct, the  $\Delta H_{ads}$  terms for adsorption steps in equilibrium (reactants or intermediates adsorbing reversibly onto the catalyst surface or active site), or others.

The exact mechanism of how the Lewis acid centers catalyze the Diels-Alder-dehydration reactions of oxygenated furans and ethylene is not clear at this time. Computational studies aimed at elucidating the role of different acid sites in

the Diels-Alder-dehydration reaction between DMF and ethylene have suggested that Lewis acids can coordinate with ethylene to catalyze the [4 + 2]-Diels-Alder reaction, but there is no prior experimental evidence of the catalysis of ethylene in Diels-Alder cycloadditions.<sup>1,2</sup> Additionally, the computational studies suggested the usefulness of Lewis acids in the dehydration of cycloadducts between ethylene and furans. Several examples of Lewis acid catalysis of dehydrative aromatizations of oxabicyclic compounds, including the use of heterogeneous Lewis acids involving Fe<sup>3+</sup>-exchanged montmorillonite K10 clay, have been reported.<sup>3-5</sup> Elucidation of the mechanism may allow for the creation of even more selective catalysts for the Diels-Alder-dehydration of the oxidized variants of HMF and ethylene for the synthesis of renewable PTA from biomass.

As mentioned, the new Diels-Alder reactions are very unusual since the furanic dienes have carboxylate group substituents that are known to typically deactivate the diene towards Diels-Alder cycloadditions. A previous system that appears to have similarities to the current Diels-Alder reactions involve 5-amino furoates reacting with mono- and deactivated dienophiles at elevated temperatures.<sup>6,7</sup> Specifically, each of these furans have an electron-donating group on the 5-position of the ring (amino-, hydroxymethyl-, methoxymethyl-, methyl-) that may help compensate the deactivating effect the carboxylate group has on the ability of the diene to react with dienophiles. Additionally, both the 5-amino furoate and HMFA/MMFC/MFA/MMF furoates not only require temperatures that are higher than usual for Diels-Alder chemistry (the 5-amino furoates react at 80°C and the HMFA/MMFC/MFA/MMF furoates react at

>170°C), but also involve a subsequent reaction that occurs in tandem. The 5-amino furoates react with dienophiles and spontaneously ring-open to generate cyclohexadienols, while the HMFA/MMFC/MFA/MMF furoates react with ethylene in the presence of a solid Lewis acid to form the dehydrated Diels-Alder adducts (1,4-substituted benzenes). Interestingly, when the cyclohexadienols were contacted with a Lewis acid ( $\text{BF}_3 \bullet \text{OEt}_2$ ) the dehydration to the polysubstituted aniline product occurred.

## 8.2 Future research directions

Currently, the key issues regarding the new Diels-Alder pathways to PTA from oxidized derivatives of HMF and ethylene that are hindering the commercial viability include slow reaction rates and low product yields (~25% MMBC yield after several hours), and low reaction concentrations (2 wt%). The conversion of DMF and ethylene to PX is currently being pursued commercially. Methods are reported in the patent application for producing high yields (>80%) of PX within several hours using DMF concentrations of up to 9 wt%.<sup>8</sup> Further research is required to develop reaction conditions, methods, and catalysts for producing the PTA intermediates (HMBA or MMBC) at yields and concentrations closer to those reported for the DMF/PX system. Since the reduction of HMF to DMF is not required for the new pathways, the yields and concentrations may not need to be as high as those for the DMF/PX system to be competitive. Although the selectivity for the MMFC/MMBC conversion using Zr-Beta is high (>70-80 %), the development of preparation methods for catalysts that allow for selectivities even closer to 100% would also be important. To improve the catalysis of the new Diels-Alder-dehydration reactions, future research efforts should be aimed at improving the understanding of (1) the reaction mechanism, including rate-determining step, and (2) the nature of the catalytic active site and deactivation mechanisms. This work will prove helpful in designing faster, more robust, and more selective catalysts.

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