

CHAPTER 3

LEWIS ACID MOLECULAR SIEVES AS DIELS-ALDER CYCLOADDITION CATALYSTS: REACTION OF FURAN WITH ACRYLIC ACID

3.1 Diels-Alder cycloaddition between furan and acrylic acid

The Diels-Alder reaction between furan and acrylic acid was studied using the series of Lewis acid molecular sieves as catalysts. These molecular sieve materials have not been previously reported as Diels-Alder catalysts, and so the aim of this work was to investigate the usefulness of these materials for improving the rates of the cycloaddition reaction. The target reaction is shown in Fig. 3.1 and did not involve the dehydration of the Diels-Alder adduct to the aromatic product, benzoic acid.

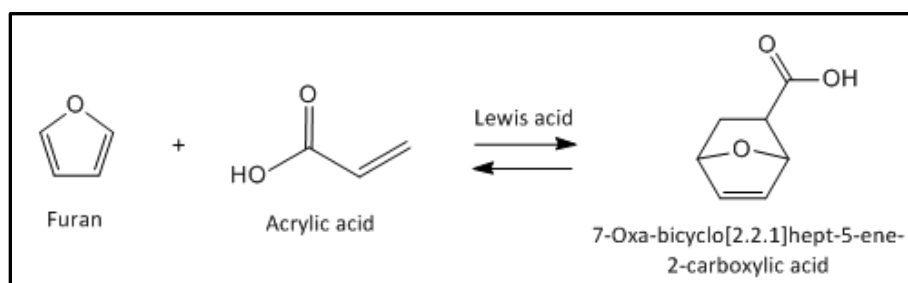


Fig. 3.1 Lewis acid-catalyzed Diels-Alder cycloaddition between furan and acrylic acid.

Lewis acid-containing solids are known to catalyze Diels-Alder reactions.¹ For example, Corma et al. have studied the Diels-Alder cycloaddition between cyclopentadiene and p-benzoquinone catalyzed by a series of silica-based Lewis acid-containing solids similar to the of Lewis acid molecular sieves that are

proposed here, that is Sn- and Ti-containing MCM-41 and ITQ-2.² MCM-41 is a mesoporous silica and ITQ-2 is a delaminated zeolitic material.

Molecular sieves can have both acid catalysis² and molecular confinement³ effects on improving rates and selectivities. Since these cycloaddition reactions are bi-molecular and have a negative change in entropy, the spatial confinement within the micropores of zeolites alone is expected to lead to improved rates.^{3,4}

The uncatalyzed cycloaddition reaction between furan and acrylic acid is very slow at ambient temperature, taking weeks to reach equilibrium conversions.⁵ It can be catalyzed by various homogenous Lewis acids, such as ZnCl_2 , FeCl_3 , AlCl_3 , and borane complexes,⁶ decreasing the time to reach equilibrium at ambient temperature to within 24 hr. When the methyl ester of acrylic acid was used as the dienophile, ZnCl_2 and ZnI_2 supported on silica gel were shown to catalyze the reaction heterogeneously.⁷

Here, Lewis acid Beta molecular sieves and scandium(III) triflate were tested as catalysts in the Diels-Alder reaction between furan and acrylic acid. Scandium(III) triflate was chosen as a reference homogeneous Lewis acid catalyst since Toste and Shiramizu successfully used scandium(III) triflate to catalyze a very similar and related Diels-Alder reaction between 2,5-dimethylfuran and acrolein.⁸

An example of the concentration profiles for furan, acrylic acid, and the Diels-Alder adduct using scandium(III) triflate as catalyst at 50°C is shown in Fig.3.2. High (>95%) selectivity to the Diels-Alder adduct was achieved and

acrylic acid conversions reached equilibrium conversions of ~40% at reaction times of 4 hours.

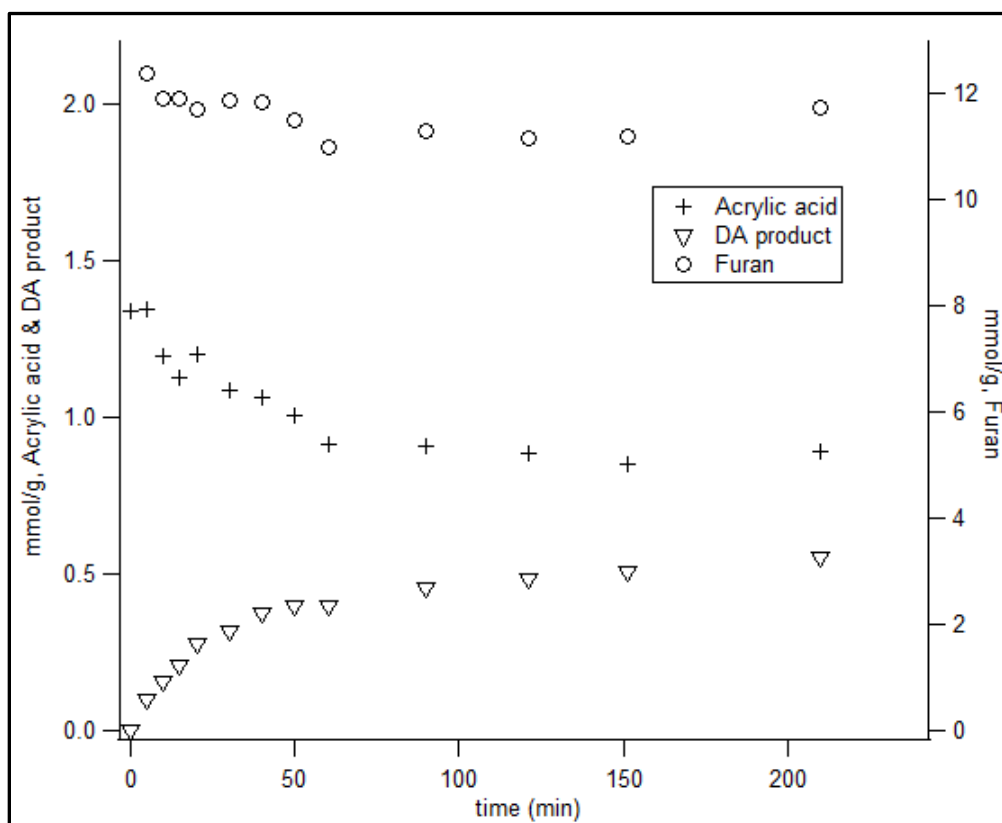


Fig. 3.2 Concentration profiles [mmol/(g solution)] of the furan and acrylic acid Diels-Alder reaction using $\text{Sc}(\text{OTf})_3$ as catalyst. Reaction conditions: $T=50^\circ\text{C}$, 3.0 g furan, 0.3 g acrylic acid, 6 mg catalyst.

Fig. 3.3 compares the Diels-Alder product concentration profiles over time for the $\text{Sc}(\text{OTf})_3$ and Lewis acid Beta molecular sieve (Sn-Beta, Zr-Beta, Ti-Beta) catalysts. A pure silica Beta molecular sieve (Si-Beta) was included as a control. The results clearly indicate that the solid Lewis acids, Sn-Beta and Zr-Beta, are catalysts for producing the Diels-Alder product and are comparable to the homogeneous Lewis acid. Ti-Beta is only marginally active when compared to

the Si-Beta control. At this reaction temperature (50°C), the dehydration of the Diels-Alder product to form benzoic acid was not observed.

This is the first time this series of Lewis acid Beta molecular sieve materials have been shown to be catalysts for any Diels-Alder reaction. In addition, this finding supports further investigation of using these materials as catalysts for the Diels-Alder reactions involving ethylene as the dienophile.

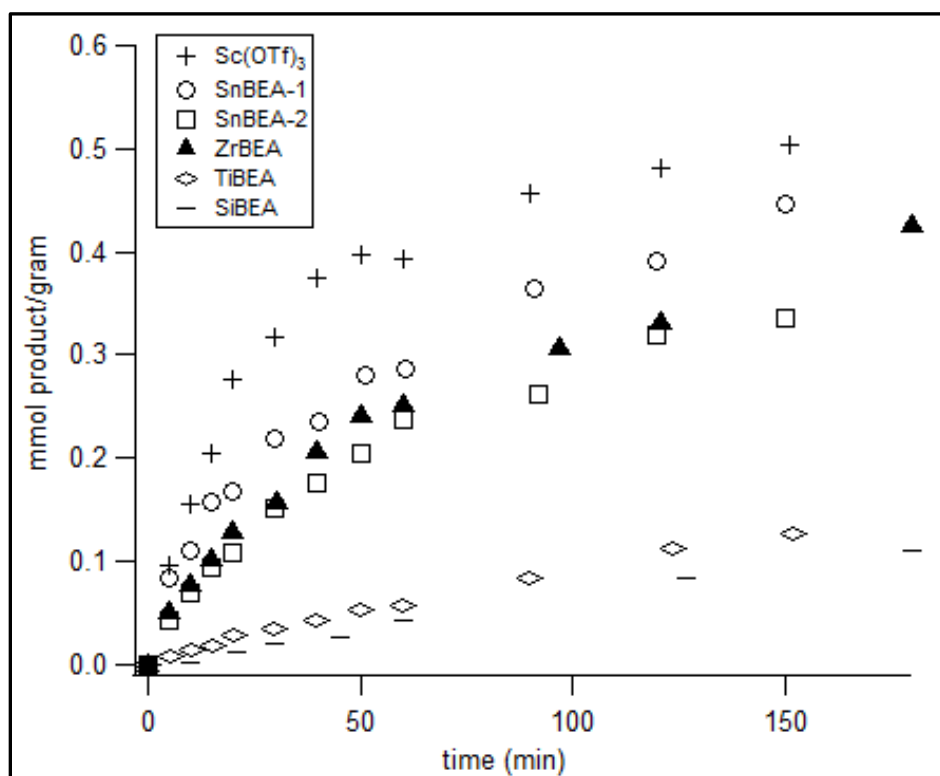


Fig. 3.3 Diels-Alder product concentration profiles using Sn-Beta, Zr-Beta, Ti-Beta, and Sc(OTf)₃ catalysts. Reaction conditions: T=50°C, 3.0 g furan, 0.3 g acrylic acid, 360 acrylic acid:metal molar ratio. Sn-BEA-2 profile used 784 acrylic acid:metal ratio.

The conversion of the Diels-Alder adduct to benzoic acid (Fig. 3.4) was not accomplished using the Sn-Beta or Zr-Beta catalysts under the reaction

conditions used for the cycloaddition, but here it is shown that the conversion can be performed using a strong Bronsted acid. Toste and Shiramizu⁸ reported methods for the conversion of a similar 7-oxabicyclo[2.2.1]hept-2-ene compound using concentrated sulfuric acid at 0°C (Fig. 3.5).

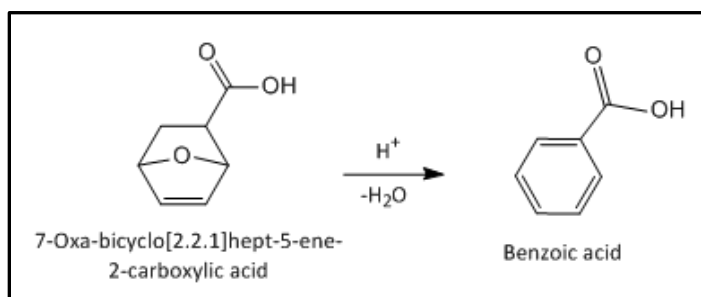


Fig. 3.4 Bronsted acid-catalyzed conversion of the Diels-Alder adduct, 7-oxa-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid, to benzoic acid.

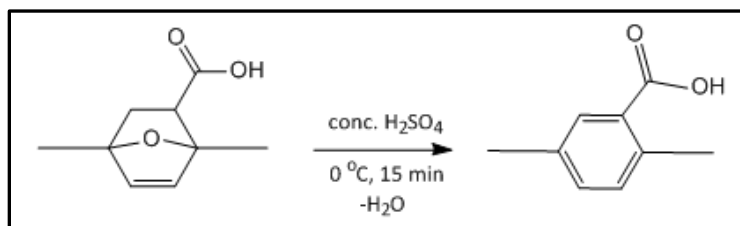


Fig. 3.5 Dehydrative aromatization example from Toste and Shiramizu.⁸

When these conditions were applied to the current Diels-Alder adduct, the formation of benzoic acid was confirmed by ¹H NMR. The product NMR spectrum obtained is given in the appendix (Fig. 3.1-A). This shows that the Diels-Alder adduct, 7-oxa-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid, is capable of undergoing dehydrative aromatization to the substituted aromatic product under strong Bronsted acid conditions at low temperatures, but the Lewis acid

Beta molecular sieves were unable to perform the dehydration under the low temperature conditions.

3.2 References

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