CHAPTER 2

MATERIALS AND METHODS FOR INVESTIGATING NEW DIELS-ALDER-DEHYDRATION ROUTES TO PTA

2.1 Preparation of catalyst materials

Three types of catalysts were chosen for investigating the Diels-Alder reactions: (1) a Bronsted acid zeolite (Al-Beta), (2) a homogeneous Lewis acid (scandium triflate, $Sc(OTf)_3$), and (3) various Lewis acid-containing silica-based molecular sieves and mesoporous silicas having the BEA, MFI and MCM-41 topologies.

The Al-Beta (or H-Beta) zeolite had a SiO_2/Al_2O_3 molar ratio of 27 and was obtained from Tosoh Corporation (Product # HSZ-930NHA). The material was received in the NH_4^+ form and calcined in air to convert to the H^+ form before use in reaction experiments.

Scandium triflate ($Sc(OTf)_3$) was used as received from Sigma-Aldrich.

Lewis acid-containing molecular sieves and mesoporous silicas were synthesized in the laboratory using the following methods:

Sn-Beta molecular sieve was prepared as follows: 7.46 g of an aqueous tetraethylammonium hydroxide (TEAOH) solution [Sigma-Aldrich, 35% (wt/wt)] was diluted with 15 g of water. 6.98 g of tetraethylorthosilicate (TEOS) [Sigma-Aldrich, 98% (wt/wt)] was added and stirred on a magnetic stirplate until the mixture became a single phase (normally, 30-90 minutes). A separate solution was prepared by dissolving 0.094 g of tin (IV) chloride pentahydrate ($SnCl_4{\cdot}5H_2O$) [Sigma-Aldrich, 98% (wt/wt)] in 1 g of water, and this solution was added dropwise to the first solution under stirring conditions. The resulting mixture was covered and stirred overnight to allow complete hydrolysis of the TEOS. The following day the desired water ratio in the gel was obtained by complete evaporation of ethanol and some water. The gel was transferred to a Teflon-liner before 0.739 g of hydrofluoric acid (HF) solution [Sigma-Aldrich, 48% (wt/wt)] was added, resulting in a thick gel with a composition of SiO_2/0.01 $SnCl_4$/0.54 TEAOH/0.54 HF/6.75 H_2O. Finally, 0.6 g of a mixture of dealuminated zeolite Beta crystals in water, prepared according to the method reported by Chang, et al.,[1] was added to the gel. The Teflon-liner was sealed in a stainless steel autoclave and heated at 140°C under rotating conditions for 5-7 days. The solids were recovered by centrifugation, washed with water (3x) and acetone (1x), and dried at 100°C overnight.

Zr-Beta molecular sieve was prepared as follows: 7.46 g of an aqueous tetraethylammonium hydroxide (TEAOH) solution [Sigma-Aldrich, 35% (wt/wt)] was diluted with 15 g of water. 6.98 g of tetraethylorthosilicate (TEOS) [Sigma-Aldrich, 98% (wt/wt)] was added and stirred on a magnetic stirplate until the mixture became a single phase (normally, 30-90 minutes). Zirconium was added to the gel as either zirconyl chloride octahydrate [$ZrOCl_2 \cdot 8\ H_2O$, Sigma-Aldrich, 98% (wt/wt)] or zirconium (IV) propoxide [Sigma-Aldrich, 70% (wt/wt) in propanol]. A separate solution was prepared by either (1) diluting zirconyl chloride octahydrate in 3-4 g of water or (2) zirconium (IV) propoxide in 2 g of ethanol, and this solution was added dropwise to the first solution under stirring conditions. Samples with gel Si/Zr = 63-400 were prepared using zirconium (IV) propoxide (Chapter 7) and the amount varied depending on the desired Si/Zr ratio. The resulting mixture was covered and stirred overnight to allow complete hydrolysis of the TEOS. The desired water ratio in the gel was obtained by complete evaporation of ethanol, propanol and some water. The gel was transferred to a Teflon-liner before 0.739 g of hydrofluoric acid (HF) solution [Sigma-Aldrich, 48% (wt/wt)] was added, resulting in a thick gel with a composition of SiO_2/0.003-0.016 ZrO_2/0.54 TEAOH/0.54 HF/6.75 H_2O. Finally, 0.6 g of a mixture of dealuminated zeolite Beta crystals in water, prepared according to the method reported by Chang, et al.,[1] was added to the gel. The Teflon-liner was sealed in a stainless steel autoclave and heated at 140^{o}C under rotating conditions for 5-7 days. The solids were recovered by centrifugation, washed with water (3x) and acetone (1x), and dried at 100^{o}C overnight.

Ta-Beta molecular sieve was prepared as follows: 7.47 g of an aqueous tetraethylammonium hydroxide (TEAOH) solution [Sigma-Aldrich, 35% (wt/wt)] was diluted with 15 g of water. 6.99 g of tetraethylorthosilicate (TEOS) [Sigma-Aldrich, 98% (wt/wt)] was added and stirred on a magnetic stirplate for 60 min. A separate solution was prepared by diluting 0.084 g $Ta(OC_2H_5)_5$ [Sigma-Aldrich, 99.98%] in 1 g of ethanol, and this solution was added dropwise to the first solution under stirring conditions. The resulting mixture was covered and stirred overnight to allow complete hydrolysis of the TEOS. The desired water ratio in the gel was obtained by complete evaporation of ethanol, propanol and some water. The gel was transferred to a Teflon-liner before 0.75 g of hydrofluoric acid (HF) solution [Sigma-Aldrich, 48% (wt/wt)] was added, resulting in a thick gel with a composition of SiO_2/0.007 TaO_2/0.54 TEAOH/0.54 HF/6.67 H_2O. Finally, 0.6 g of a mixture of dealuminated zeolite Beta crystals in water, prepared according to the method reported by Chang, et al.,[1] was added to the gel. The Teflon-liner was sealed in a stainless steel autoclave and heated at 140°C under rotating conditions for 5 days. The solids were recovered by centrifugation, washed with water (3x) and acetone (1x), and dried at 100°C overnight.

Nb-Beta molecular sieve was prepared as follows: 7.48 g of an aqueous tetraethylammonium hydroxide (TEAOH) solution [Sigma-Aldrich, 35% (wt/wt)] was diluted with 15 g of water. 6.99 g of tetraethylorthosilicate (TEOS) [Sigma-Aldrich, 98% (wt/wt)] was added and stirred on a magnetic stirplate for 65 min. A separate solution was prepared by diluting 0.099 g $Nb(OC_2H_5)_5$ [Sigma-Aldrich, 99.95%] in 1 g of ethanol, and this solution was added dropwise to the first solution under stirring conditions The resulting mixture was covered and stirred overnight to allow complete hydrolysis of the TEOS. The desired water ratio in the gel was obtained by complete evaporation of ethanol, propanol and some water. The gel was transferred to a Teflon-liner before 0.74 g of hydrofluoric acid (HF) solution [Sigma-Aldrich, 48% (wt/wt)] was added, resulting in a thick gel with a composition of SiO_2/0.01 NbO_2/0.54 TEAOH/0.54 HF/6.67 H_2O. Finally, 0.6 g of a mixture of dealuminated zeolite Beta crystals in water, prepared according to the method reported by Chang, et al.,[1] was added to the gel. The Teflon-liner was sealed in a stainless steel autoclave and heated at 140°C under rotating conditions for 5 days. The solids were recovered by centrifugation, washed with water (3x) and acetone (1x), and dried at 100°C overnight.

Ti-Beta molecular sieve was prepared as follows: 3.53 g of tetraethylammonium fluoride hydrate [Alfa Aesar, 97% (wt/wt)] was dissolved in 7 g of water. 7 g of tetraethylorthosilicate (TEOS) [Sigma-Aldrich, 98% (wt/wt)] was then added and the mixture was stirred for 30 min. A separate solution was prepared by diluting 0.123 g of titanium (IV) isopropoxide [Sigma-Aldrich, 99%] in 2 g of ethanol, and this solution was added dropwise to the first solution under stirring conditions. The resulting mixture was covered and stirred overnight to allow complete hydrolysis of the TEOS. The desired water ratio in the gel was obtained by complete evaporation of ethanol, isopropanol and some water, resulting in a gel with composition 1 SiO_2/0.013 TiO_2/0.55 TEAF/8.07 H_2O. Finally, 0.15 g of pure silicon zeolite Beta seeds was added to the gel. The gel was transferred to a Teflon-lined stainless steel autoclave and heated at 140^{o}C under static conditions for 14 days. The solids were recovered by centrifugation, washed with water (3x) and acetone (1x), and dried at 100^{o}C overnight.

Tin and aluminum-containing Beta molecular sieve (Sn-Al-Beta) was prepared as follows: 7.75 g of an aqueous tetraethylammonium hydroxide (TEAOH) solution [Sigma-Aldrich, 35% (wt/wt)] was diluted with 15.65 g of water, followed by the addition of 1.24 g of hydrogen peroxide solution [Sigma-Aldrich, 30% (wt/wt)]. 7 g of tetraethylorthosilicate (TEOS) [Sigma-Aldrich, 98% (wt/wt)] was added and stirred on a magnetic stirplate for about 30 min. A separate solution was prepared by dissolving 0.113 g of tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) [Sigma-Aldrich, 98% (wt/wt)] in 1 g of water, and this solution was added dropwise to the first solution under stirring conditions. After about 20 min of stirring, 0.056 g of aluminum isopropoxide powder was added to the gel while stirring. The resulting mixture was covered and stirred overnight to allow complete hydrolysis of the TEOS. The desired water ratio in the gel was obtained by complete evaporation of ethanol, isopropanol and some water. The gel was transferred to a Teflon-liner before 0.74 g of hydrofluoric acid (HF) solution [Sigma-Aldrich, 48% (wt/wt)] was added, resulting in a thick gel with a composition of SiO_2/0.01 SnO_2/0.0042 Al_2O_3/0.56 TEAOH/0.56 HF/7.22 H_2O. Finally, 0.6 g of a mixture of dealuminated zeolite Beta crystals in water, prepared according to the method reported by Chang, et al.,[1] was added to the gel. The Teflon-liner was sealed in a stainless steel autoclave and heated at 140^oC under rotating conditions for 8 days. The solids were recovered by centrifugation, washed with water (3x) and acetone (1x), and dried at 100^oC overnight.

Sn-MCM-41 was prepared as follows: 1.98 g of hexadecyltrimethylammonium bromide (CTAB) [Sigma-Aldrich, 98% (wt/wt)] was dissolved in 10 g of water. Next, 3.15 g of tetramethylammonium hydroxide solution (TMAOH) [Sigma-Aldrich, 25% (wt/wt) in water] was added. A separate solution was prepared by diluting 0.12 g of tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) [Sigma-Aldrich, 98% (wt/wt)] in 1.89 g of water, and this solution was added dropwise to the first solution under stirring conditions. Finally, 2 g of fumed silica [Cab-O-Sil EH-5, 99.9% purity] was added, resulting in a thick gel with composition 1 SiO_2/0.01 $SnCl_4$/0.16 CTAB/0.26 TMAOH/24.3 H_2O. The homogeneous gel was transferred to a Teflon-lined stainless steel autoclave and heated at 140^oC under static conditions for 25 hours. The solids were recovered by centrifugation, washed with water (3x) and acetone (1x), and dried at room temperature under flowing air.

Zr-MCM-41 was prepared as follows: 1.98 g of hexadecyltrimethylammonium bromide (CTAB) [Sigma-Aldrich, 98% (wt/wt)] was dissolved in 10 g of water. Next, 3.15 g of tetramethylammonium hydroxide solution (TMAOH) [Sigma-Aldrich, 25% (wt/wt) in water] was added. A separate solution was prepared by diluting 0.055 g of zirconyl chloride octahydrate [$ZrOCl_2$ ▪ 8 H_2O, Sigma-Aldrich, 98% (wt/wt)] in 2.13 g of water, and this solution was added dropwise to the first solution under stirring conditions. Finally, 2 g of fumed silica [Cab-O-Sil M5, 99.9% purity] was added, resulting in a thick gel with composition 1 SiO_2/0.005 ZrO_2/0.16 CTAB/0.26 TMAOH/24.3 H_2O. The homogeneous gel was transferred to a Teflon-lined stainless steel autoclave and heated at 140^oC under static conditions for 22 hours. The solids were recovered by centrifugation, washed with water (3x) and acetone (1x), and dried at room temperature under flowing air.

An amorphous SiO_2 material containing Sn^{4+} (Sn-SiO_2) was prepared by a xerogel method: 6.989 g of tetraethylorthosilicate (TEOS) [Sigma-Aldrich, 98% (wt/wt)] was diluted with 8.682 g of water. 1.904 g of HCl solution (J.T. Baker, 0.1 N) was added and the resulting solution was stirred for 2 hours. Next, a second solution of 0.199 g of tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) [Sigma-Aldrich, 98% (wt/wt)] in 2 g of water was prepared and added dropwise to the first solution. After an additional hour of stirring, a tetrapropylammonium hydroxide

(TPAOH) solution [Alfa Aesar, 40% (wt/wt)] was added dropwise until the gel hardened to a soft, colorless solid. The hardened gel was allowed to dry in a 100^{o}C oven overnight to produce the “as-made” xerogel solid. The resulting solid was calcined at 580^{o}C for 6 h.

Sn-MFI was prepared using a solid transformation of the “as-made” xerogel solid described above in the synthesis of the amorphous Sn-SiO_2 material: A tetrapropylammonium hydroxide (TPAOH) solution [20% (wt/wt)] was prepared by diluting a 40% (wt/wt) TPAOH solution (Alfa Aesar) with water. The 20% (wt/wt) TPAOH solution was added to the “as-made” xerogel solid (described above) in a ratio of 1.6 g TPAOH (20%) : 1 g xerogel solid, and this mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 175^{o}C under static conditions for 24 hours. The solids were recovered by centrifugation, washed with water (3x) and acetone (1x), and dried at 100^{o}C overnight.

Zr-MFI was prepared as follows: 7.36 g of tetrapropylammonium hydroxide (TPAOH) solution [20% (wt/wt)] was diluted in 22.05 g of water. Next, 7 g of tetraethylorthosilicate (TEOS) [Sigma-Aldrich, 98% (wt/wt)] was added and the solution was stirred for 30 min. A separate solution was prepared by diluting 0.085 g of zirconyl chloride octahydrate [$ZrOCl_2 \cdot 8\ H_2O$, Sigma-Aldrich, 98% (wt/wt)] in 4 g of water, and this solution was added dropwise to the first solution under stirring conditions. The resulting mixture was covered and stirred overnight to allow complete hydrolysis of the TEOS. The desired water ratio in the gel was obtained by complete evaporation of ethanol and some water, resulting in a gel with composition 1 SiO_2/0.008 ZrO_2/0.44 TPAOH/30 H_2O. The gel was transferred to a Teflon-lined stainless steel autoclave and heated at 180^{o}C under static conditions for 48 hours. The solids were recovered by centrifugation, washed with water (3x) and acetone (1x), and dried in a 100^{o}C oven overnight.

All materials were calcined in a muffle furnace with flowing air (breathing grade). The as-made material was placed in a ceramic dish and heated in the oven using the following temperature program: ramp at 1^{o}C/min from ambient to 150^{o}C and hold for 3 hours, followed by ramping at 1^{o}C/min from 150^{o}C to 580^{o}C and holding for 6 hours.

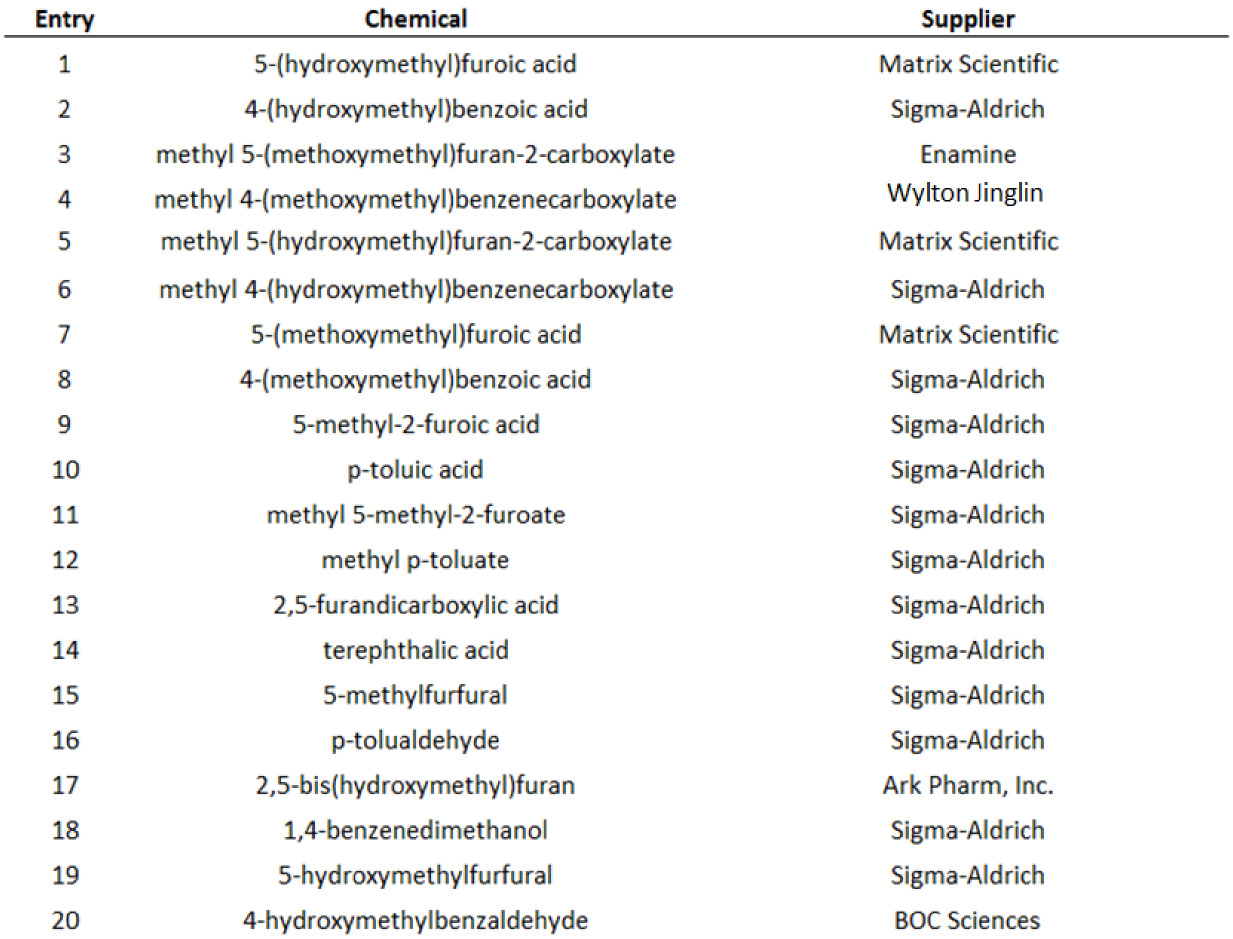
2.2 Characterization of materials

Powder x-ray diffraction (XRD) patterns of the synthesized materials confirmed the BEA, MFI, and MCM-41 topologies and indicated high crystallinity of the samples. XRD patterns were collected using a Rigaku Miniflex II diffractometer and Cu Kα radiation. See Figures 2.1-A to 2.5-A in the appendix for XRD patterns.

Scanning electron microscopy (SEM) images with energy dispersive x-ray spectroscopy (EDS) measurements were used to determine crystal size and silicon/metal (Si/M) atom ratios, respectively. SEM and EDS were recorded on a LEO 1550 VP FE SEM at an electron high tension (EHT) of 15 or 20 kV.

2.3 Suppliers for furans and other organic reagents

Table 2.1 List of suppliers for dienes and Diels-Alder-dehydration product standards.



Entry	Chemical	Supplier
1	5-(hydroxymethyl)furoic acid	Matrix Scientific
2	4-(hydroxymethyl)benzoic acid	Sigma-Aldrich
3	methyl 5-(methoxymethyl)furan-2-carboxylate	Enamine
4	methyl 4-(methoxymethyl)benzenecarboxylate	Wylton Jinglin
5	methyl 5-(hydroxymethyl)furan-2-carboxylate	Matrix Scientific
6	methyl 4-(hydroxymethyl)benzenecarboxylate	Sigma-Aldrich
7	5-(methoxymethyl)furoic acid	Matrix Scientific
8	4-(methoxymethyl)benzoic acid	Sigma-Aldrich
9	5-methyl-2-furoic acid	Sigma-Aldrich
10	p-toluic acid	Sigma-Aldrich
11	methyl 5-methyl-2-furoate	Sigma-Aldrich
12	methyl p-toluate	Sigma-Aldrich
13	2,5-furandicarboxylic acid	Sigma-Aldrich
14	terephthalic acid	Sigma-Aldrich
15	5-methylfurfural	Sigma-Aldrich
16	p-tolualdehyde	Sigma-Aldrich
17	2,5-bis(hydroxymethyl)furan	Ark Pharm, Inc.
18	1,4-benzenedimethanol	Sigma-Aldrich
19	5-hydroxymethylfurfural	Sigma-Aldrich
20	4-hydroxymethylbenzaldehyde	BOC Sciences

2.4 Methods for studying the Diels-Alder reaction between furan and acrylic acid

The Diels-Alder cycloaddition reaction between furan and acrylic acid was investigated using the Lewis acid Beta molecular sieves and scandium triflate homogeneous Lewis acid as catalysts. The reactions were performed in batch operation and the liquid phase was analyzed using quantitative ^{1}H NMR. Reaction experiments were conducted in a thick-walled glass reactor with a crimp-top seal. The glass reactor was loaded with a magnetic stir bar, catalyst, and 3 grams (44 mmol) of furan (Sigma-Aldrich). The catalyst amount was added to meet a target molar ratio of ~360 acrylic acid:metal atoms. Next, 0.3 grams (4.2 mmol) of acrylic acid (Sigma-Aldrich) was added, and the reactor was immediately sealed and placed in a 50^{o}C water bath. The reaction system was under autogeneous pressure due to the low boiling point (32^{o}C) of the furan solvent/reactant. Aliquots (20 μl) were collected at different times during the reaction by using a syringe needle through the crimp-top seal. Each aliquot was diluted in a known mass of $CDCl_3$ containing a known concentration of tetraethylsilane (TES) as external standard, transferred to an NMR tube through a filter pippette (to remove the solid catalyst), and a ^{1}H NMR spectrum was collected at room temperature. Figure 2.6-A in the appendix shows an example ^{1}H NMR spectrum of the product solution of the Diels-Alder (DA) reaction between furan and acrylic acid with each of the peaks identified. By using the tetraethylsilane peaks, the acrylic acid and DA product concentrations in the furan solvent/reactant were measured.

The DA product, 7-oxa-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid, was dehydrated to the aromatic product, benzoic acid, by treatment with concentrated sulfuric acid. The procedure was adapted from Shiramizu and Toste.[2] In a small screwtop sample vial, concentrated sulfuric acid (98%, 400 μl) was added to the solid DA product (30 mg, Matrix Scientific) while stirring in an ice bath. After 15 minutes, the reaction mixture was quenched with an aqueous sodium bicarbonate solution. The organic products were extracted several times with ethyl acetate, and the organic phases were combined into a round bottom flask. The mixture was dried with addition of magnesium sulfate, the solids separated by filtration, and the ethyl acetate and other volatiles were removed by rotary evaporation. The remaining solids were dissolved in $CDCl_3$ and the ^1H NMR spectrum was taken at room temperature.

2.5 Methods for studying Diels-Alder-dehydration reactions using ethylene and various substituted furans

High-pressure ethylene gas was used in the screening of Diels-Alder-dehydration reactions with various furanic dienes. Experiments were carried out in a 50 ml high-pressure stainless steel batch reactor (Parr Series 4590) equipped with a magnetic stirrer and heater. The o-ring material that was chosen to seal the reactor cylinder to the reactor head was Kalrez® Sprectrum^{TM} 7090 perfluoroelastomer. The reactor setup allowed for ethylene gas (Matheson, 1200 psig, 99.995% purity) or helium to be charged to the reactor. A high-pressure oxygen/moisture trap (Agilent OT3) was also installed on the inlet line.

In a typical experiment, the catalyst and reaction solution were loaded into the Parr reactor. About 10 ml of reaction solution were used in the experiments since this was the minimal volume that allowed for contact of the stirrer with the liquid. This ensured mixing during the reactions while minimizing the usage of catalyst and reagent. If a quantitative analysis of the reaction was being performed, an initial aliquot (~0.5 g) of the feed solution was collected and analyzed with the final product solution after reaction. The magnetic stirrer was operated at ~200 rpm and the head space of the reactor was purged with helium gas with a fill/vent cycle (10x). Next, the reactor was pressurized to ~10-40 bar (room temperature) with ethylene gas, the inlet valve was closed, and the reaction was performed in batch operation. The reactor was heated to the reaction temperature (150-300^{o}C) while the pressure increased autogenously. For example, when the reactor was pressurized to 37 bar and heated to 190^{o}C, the pressure increased autogenously to 70 bar. At the end of the reaction time, the reactor was allowed to cool to room temperature and the reactor gases were vented. The reactor vessel was opened and the liquid/solids were then collected into a 20 ml glass scintillation vial before analysis by ^{1}H NMR, GC/FID, GC/MS, and/or HPLC.

Before each experiment, the reactor was cleaned using the following procedure. The Parr reactor cylinder, stirrer, thermocouple, inlet diptube, and o-ring were cleaned by hand with acetone and Kim-Wipe. Then, about 25 ml of the solvent that was planned for use in the next experiment was added to the reactor and sealed to the head. For example, if dioxane was planned to be used in the next experiment, dioxane was used in this step. The reactor was purged with helium gas with a fill/vent cycle (10x). This process was performed in order to make an effort to rinse clean the inlet diptube of the reactor head and replace any residual liquid in the diptube with the same solvent that was being used for the next experiment. Following the fill/vent cycle, the reactor was opened and the cylinder was emptied and rinsed clean with acetone and Kim-Wipe.

2.6 Analysis of ethylene/furan Diels-Alder products by ^{1}H NMR

The liquid product solutions were analyzed by ^{1}H NMR to identify products (by comparing to known product standards) and to quantify conversion, product yield, and selectivity. This analysis method was used primarily in the exploratory portion of the project due to the convenience of the method, particulary when analyzing a variety of reactions during screening investigations.

Typically, an aliquot (~ 0.2 g) of the crude product mixture was diluted in $CDCl_3$ or DMSO-d_6 NMR solvent (~1.0 g) and transferred to an NMR tube using a filter pipette to remove catalyst and/or any solid reaction products. The ^{1}H NMR spectrum was collected at room temperature. If a quantitative analysis was being performed, the NMR solvent contained tetraethylsilane (TES) as external standard at a known concentration. Both the feed solution and product solution were analyzed to determine reactant and product concentrations and conversion, product yield, and selectivity. For example, the signals used for calculating the conversion of methyl 5-methoxymethyl-furan-2-carboxylate (MMFC) and the yield of methyl 4-(methoxymethyl)benzene carboxylate (MMBC) in DMSO-d_6: tetraethylsilane δ = 0.49 ppm (q, 8 H); MMFC δ = 6.63 ppm (d, 1 H) and δ = 7.26 ppm (d, 1 H); MMBC δ = 7.46 ppm (d, 2 H) and δ = 7.95 ppm (d, 2 H).

During the course of investigating the Diels-Alder-dehydration reaction between MMFC and ethylene to produce MMBC, an alternative technique to quantify the reaction results using ^{1}H NMR was also used. Rather than using TES as external standard, it was found that the dioxane solvent could be used as an internal standard reference. The procedure involved simply calculating the area ratios of the MMFC [δ = 6.63 ppm (d, 1 H) and δ = 7.26 ppm (d, 1 H)] and MMBC [δ = 7.46 ppm (d, 2 H) and δ = 7.95 ppm (d, 2 H)] peaks to the dioxane solvent peak for both the feed and product solutions, and measure the MMFC conversion and MMBC yield by comparing these area ratios. This method was used for determining the reaction results in Table 5.5. Fig. 2.7-A in the appendix shows the use of the dioxane peak in the ^{1}H NMR as internal standard reference gives accurate determination of MMFC and MMBC concentrations in dioxane for a series of calibration solutions of known concentrations. Table 2.1-A compares reaction results measured using the TES external standard and the dioxane solvent as internal standard, showing that both methods give similar results.

2.7 Analysis of reaction products by GC/FID

GC/FID analysis was performed on an Agilent 7890B GC system equipped with a flame ionization detector (FID). The column used was an Agilent HP-5 (30 m x 0.32 mm x 0.25 µm) with N_2 as carrier gas (6 ml/min flow through column). The injection samples were typically prepared by filtering a small aliquot of the product solution through a filter pipette before diluting in dichloromethane (DCM) in a ratio of 30 mg sample:170 mg of DCM. Volumes of 1 µL were injected into the GC using a Hamilton 5 µL GC injection syringe. Split mode was used with a 7:1 split ratio. A typical oven temperature program was as follows: Hold 75^{o}C for 0.3 min, ramp to 90^{o}C at 10^{o}C/min and hold for 4.5 min, ramp to 300^{o}C at 50^{o}C/min and hold for 3 min.

2.8 Analysis of reaction products by GC/MS

GC/MS analysis was performed on an Agilent 5890 GC interfaced with a 5970 Mass Selective Detector. The column used was an DB-5 (30 m x 0.25 mm x 0.25 µm). The MSD was set to scan 50 to 550 m/z at 1.61 scans/s. The ionization mode was electron ionization and the instrument was tuned using standard manufacturer autotune procedures using PFTBA (perfluorotributylamine) standard.

GC/TOF-MS analysis was performed by JEOL on a AccuTOF GCv 4G system. The MS ion source was a EI/FI/FD Combination Ion Source (EI+: 70eV, 300µA, 280 ^{o}C; FI+: -10kV, 40mA(30msec), JEOL emitter, Heater OFF). GC-interface temperature of 280^{o}C used with 1 Hz data acquisition rate.

2.9 Analysis of reaction products by HPLC

HPLC separation and analysis was performed on an Agilent HPLC system with an Agilent Hi-Plex H column using a pure water mobile phase flowing at 0.6 ml/min. The column temperature was held at 65^{o}C. The injection samples were prepared by transferring a small aliquot through a 0.2 μm filter into an HPLC vial (Waters), and injection volumes of 2 μL were used. A diode array detector (DAD) was used with wavelength signals of 205 and 228 nm.

2.10 References

[1] Chang, C-C.; Wang, Z.; Dornath, P.; Cho, H.J.; Fan, W.; *RSC Adv.* **2012**, *2*, 10475 – 10477

[2] Shiramizu, M.; Toste, F.D.; *Chem. Eur. J.* **2011**, *17*, 12452 – 12457.