

Supporting Information:

Biomass-Derived Butadiene by Dehydra-Decyclization of Tetrahydrofuran

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1.0 Materials

1.1 Reagents and standard chemicals:

Tetrahydrofuran (Certified grade, Fisher Chemical), 2-methyl-tetrahydrofuran (2-MTHF, >99.5 %, Sigma-Aldrich) and 2,5-dimethyl-tetrahydrofuran (2,5-DMTHF mixture of *cis* and *trans*, 96 %, Sigma-Aldrich) were used in the vapor-phase dehydra-decyclization to produce C₄, C₅ and C₆-dienes. Standard chemicals including 1,3-butadiene (>99 %), isoprene (>99 %), 1,4-pentadiene (>99 %), 1,5-hexadiene (97 %), 1,4-hexadiene (mixture of *cis* and *trans*, 99 %), 1,3-hexadiene (mixture of *cis* and *trans*, 95 %) and 2,4-hexadiene (mixture of *cis* and *trans*, 90 %) were purchased from Sigma-Aldrich.

1.2 Catalysts

A variety of commercial catalysts were utilized in the vapor phase dehydra-decyclization including H-Y zeolite (Zeolyst CBV760, Si/Al = 30), ZSM-5 zeolite (Zeolyst CBV28014, Si/Al ratio = 140), sodium phosphate (Na₃PO₄, Sigma Aldrich), silica alumina (SiAl, Sigma Aldrich), niobium oxide (Nb₂O₅, Sigma Aldrich), zirconium oxide (ZrO₂, Sigma Aldrich), phosphotungstic acid (H₃PW₁₂O₄₀, PWA, Sigma Aldrich). In addition to commercially available catalysts, Sn-BEA and various phosphorous containing zeolites were prepared in house. Details of the preparation methods are provided in subsequent sections.

2.0 Catalyst Synthesis

2.1 *P-BEA*

P-BEA was synthesized according to the literature [34]. Commercial zeolite Al-BEA (Zeolyst CP814E, Si/Al = 12.5) was dealuminated by treatment with 70 wt % nitric acid (HNO_3 , Fisher Scientific). Typically, 0.5 g of the Al-BEA was mixed with 25 mL of 70 wt % HNO_3 in a Teflon-lined stainless steel autoclave. The autoclave was then put into an oven at 80 °C for 24 h under a static condition. The dealuminated zeolite BEA (DeAl-BEA) was washed extensively with deionized water and dried overnight at 100 °C. In order to prepare P-BEA with Si/P = 27 (confirmed by ICP analysis), wet impregnation was performed by stirring 0.4 g of DeAl-BEA and 18.2 μL of 85 wt% phosphoric acid (H_3PO_4 , Sigma-Aldrich) in 3.33 mL of deionized water. The impregnated sample was dried at 90 °C overnight, followed by calcination in a tube furnace with dry air at 600 °C for 25 min.

2.2 *P-Al-BEA*

P-Al-BEA was prepared by impregnation of H_3PO_4 on zeolite Al-BEA (Zeolyst, CP814E, Si/Al = 12.5), according to the same procedure described in the preparation of P-BEA, without the dealumination step.

2.3 *P-SPP*

P-SPP with Si/P = 27 (confirmed by ICP analysis) was synthesized according to the literature [34]. Typically, tetra(n-butyl) phosphonium hydroxide (TBPOH, 40 wt %, Sigma-Aldrich) as a structure-directing agent (SDA) was added dropwise into tetraethylorthosilicate (TEOS, 98%, Sigma-Aldrich) under stirring. Deionized water was then added to this mixture, and

stirred for 24 h. The mixture became a clear sol with a composition of 1 SiO₂ : 0.3 TBPOH : 10 H₂O : 4 EtOH. The sol was sealed in a Teflon lined stainless steel autoclave and heated for 3 days in an oven at 115 °C. After crystallization, the solid product was extensively washed with deionized water by centrifugation and decanting of the supernatant. This process 3 was repeated until the pH of the final supernatant was lower than 9. Subsequently, the collected sample was dried at 90 °C overnight and calcined in a tube furnace at 550 °C for 12 h under dry air.

2.4 P-MFI

First, pure silica zeolite Si-MFI with a composition of 1 SiO₂ : 0.26 TPAOH : 15 H₂O : 4 EtOH was synthesized by mixing structure directing agent tetrapropylammonium hydroxide solution (TPAOH, 40 wt%, SACHEM), water and tetraethylorthosilicate (TEOS, 98%, Sigma-Aldrich). The mixed gel was sealed in a Teflon lined stainless steel autoclave and heated for 3 days in an oven at 180 °C. The solid products were centrifuged, washed with distilled water (until pH<8) and then dried at 70 °C overnight and calcined at 550 °C for 6 h in air under static conditions. In order to prepare P-MFI with similar P content as P-BEA, the same wet impregnation procedure was performed for P-MFI as in preparation of P-BEA. First, 0.4 g of Si-MFI, 18.2 µL of 85wt % phosphoric acid (H₃PO₄, Sigma-Aldrich) and 3.33 mL of deionized water were mixed. Then, the impregnated sample was dried at 90 °C overnight, followed by calcination in a tube furnace with dry air at 600 °C for 25 min.

2.5 Pelletization procedure

In order to maintain a relatively uniform particle distribution and avoid excessive pressure drops, catalyst powders utilized in the microcatalytic and packed bed reactors were pelletized to achieve a particle diameter of 500-1000 µm. Briefly, 100-200 mg of catalyst powder were placed

into a 13 mm pellet press (Pike technologies) and pressed to 2 tons of pressure, holding for 10-15 mins. The catalyst pellet was then extracted and broken up into smaller particles, which were then passed through a set of sieves from which the 500-1000 μm sieve cut was collected and used for catalytic testing throughout the study.

3.0 Catalyst Characterization

Textural information of the various catalysts employed in this study was characterized through Ar physisorption in an Autosorb iQ2 porosimetry instrument (Quantachrom). Prior to analysis, catalysts were outgassed at 573 K for 6 hours and subsequently cooled down to room temperature under vacuum. BET specific surface area measurements were used to represent the total surface area of the catalyst materials; total pore volume was determined using a single point measurement at $P/P_0 = 0.97$. Brønsted acid site concentration (H^+) was determined by isopropylamine temperature programmed desorption (IPA-TPD). Catalyst samples were dehydrated at 400 °C under a stream of He for one hour then allowed to cool down to 120 °C where the catalyst was contacted with IPA for 15 minutes. The catalyst was then held under a stream of He for one hour to remove any physisorbed IPA, after which the temperature was ramped at a rate of 10°C/min to 700 °C. IPA-TPD was not conducted for the phosphorous containing materials, since earlier studies with P-containing materials did not result in any detectable acidity^[34].

Table S1. Catalyst Characteristics.

| Catalyst | Surface Area (m ² g ⁻¹) | Pore Volume (cm ³ g ⁻¹) | Si:Al ^a | H ⁺ (μmol g ⁻¹) |
|--------------------------------|--|--|--------------------|--|
| H-Y | 720 | 0.36 | 30 | 350 |
| ZSM-5 | 400 | 0.19 | 140 | 90 |
| SiAl | 276 | 0.68 | 13 | 377 |
| Sn-BEA | 637 | 0.33 | - | - ^b |
| Nb ₂ O ₅ | 8 | 0.07 | - | 30 |

a- Provided by the manufacturer

b- Cannot be determined by existing methods

Table S2. Phosphorous-containing Catalyst Characteristics.

| Catalyst | Surface Area (m ² g ⁻¹) | Pore Volume (cm ³ g ⁻¹) | Si:P ^a |
|----------|--|--|-------------------|
| P-SPP | 598 | 1.11 | 27 |
| P-BEA | 499 | 0.80 | 27.1 |
| P-MFI | 416 | 0.25 | 27 |
| P-Al-BEA | 552 | 0.84 | 27 |

a- Determined by ICP-MS

3.1 ICP-MS

Elemental analysis was performed on inductively coupled plasma optical emission spectroscopy (ICP-OES, iCap 6500 Dual view, Thermo Scientific) in the Analytical Geochemistry Lab, Department of Earth Sciences at the University of Minnesota.

4.0 Reaction Methods: Flow reactor

The steady state measurements of the dehydra-decyclization of THF, 2-MTHF and 2,5-DMTHF to their respective dienes over solid acid catalysts was performed in a downflow packed bed reactor. Liquid compounds were fed into a vaporization section through a 1/16" PEEK capillary line (0.01" ID), where a syringe pump (KDS-100, KD Scientific) equipped with a gas tight syringe (Hamilton Company) controlled the liquid flow rate. The vaporization section consisted of an insulated aluminum tube wrapped with a heating tape, inside where the liquid feed was vaporized and swept with a helium carrier gas regulated by a mass flow controller (Brooks, 5850S). Helium flow rates were adjusted according to desired reaction conditions anywhere between 30-100 sccm. The vaporized stream of reactants in helium was then passed through a switching section, consisting of a heated 6-port valve (Vici Valco, DL6UWE), from which the stream could be sent either directly to the analysis section or through the reactor first. Details of the possible flow patterns are illustrated in Figure S1. The reactor consisted of a 1/2" 316 SS tube packed with quartz chips and catalyst operated in a down flow mode at 1.1 bar. The pressure drop across the catalyst bed was maintained below 5% of the total pressure, achieved by maintaining the catalyst particle diameter between 500-1000 μm . The catalyst bed was placed between two plugs of inert quartz wool, above which the void volume was reduced using inert quartz packing in the range of 850-4750 μm (Sigma Aldrich). Temperature measurements were made using a 1/16" type-K thermocouple (Omega) placed directly below the catalyst bed, while a second thermocouple was placed in the furnace used to control the temperature using a PID temperature controller (OMEGA,CN-7800). Prior to introducing any reactant, the catalyst bed was heated at 3 K min⁻¹ to 673 K and held for 1 hour under a 50 sccm stream of air. The catalyst bed was then cooled down to the desired reaction temperature and flushed with a stream of He prior to

introducing the vapor phase reactant stream. Analysis of the vapor phase products was performed using an online gas sampling gas chromatograph (Agilent, 7890A) equipped with a quantitative carbon detector (QCD, POLYARC) in conjunction with a flame ionization detector (FID). Separation of the various products and reactant in the GC were performed using an HP-PLOT Q column (Agilent, 19091P-QO4).

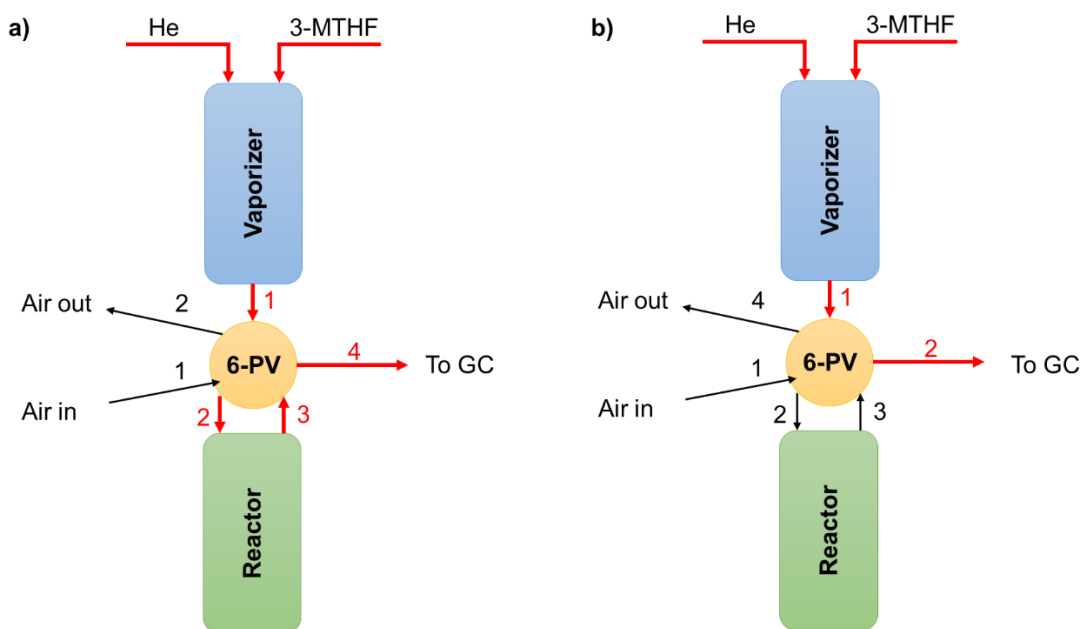


Figure S1. Schematic of the Packed Bed Catalyst Flow Reactor. (a) Reaction Configuration. (b) Reactor bypass configuration.

5.0 Reaction Methods: Microcatalytic reactor

Reactions to screen for catalysts and operating conditions were performed in a microcatalytic reactor. The reactor consists of a glass reactor (i.e., inlet liner) placed in the inlet of a gas chromatograph (Aglient 7890A). The reactor was packed with quartz wool below (7.5 mg) and above (15 mg) the catalyst (~45 mg). A diagram of the reactor is shown in Figure S2 below:

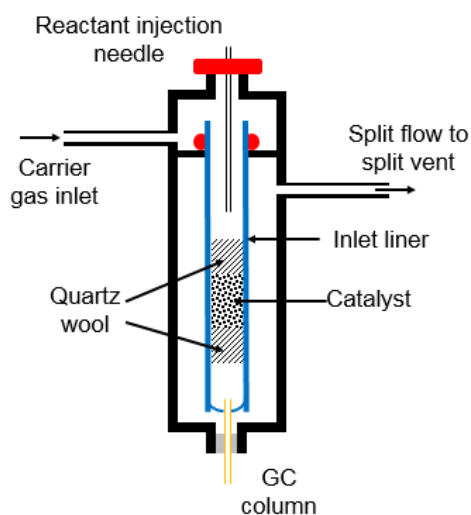


Figure S2. Diagram of high throughput pulsed flow reactor (HTPFR) implementing the ‘microcatalytic’ method.

Experiments were performed at reaction temperatures of 200 to 400 °C. The space velocity was controlled by adjusting the carrier gas (He, 99.999%) flow rate to the split vent. Space velocities of 0.2 – 130 s⁻¹ were tested with the reactor, where space velocity is defined as follows:

$$S = \text{space velocity} = \frac{F_{\text{He}}}{V_C} [=] \text{min}^{-1} \quad (\text{S1})$$

where F_{He} is the flow rate of He through in sccm min⁻¹ and V_C is the volume of the catalyst bed. Helium pressure was kept constant at 15-30 psi during a reaction. Each experiment was performed by injecting 1 uL of pure reactants into the reactor followed by immediate separation and quantification of the products. Reaction products were separated using a chromatographic column

(Agilent, HP-Plot Q, 30 m, 0.32 mm ID, 20 μ m film thickness; temperature program: 40 °C for 2 min, 10 °C/min to 270 °C, hold 10 min) followed by quantification using a quantitative carbon detector (Polyarc/FID).

6.0 Thermodynamic Calculations

All calculations were performed with the Gaussian 09 (Rev. C.1) program in the gas phase with the CBS-QB3 Complete Basis Set method [35]. Vibrational frequencies, rotational temperature, electronic energy, among other values calculated by Gaussian for each molecule are used to calculate first, partition functions and finally thermochemical data resulting in Gibbs Free energies. Each calculation took into account contributions from translational, rotational, electric, and vibrational energies to determine the overall partition function. Theory and guidelines of this process can be found in the cited resource by Ochterski [36].

The CBS-QB3 method was chosen due to its agreement (+ 1 kcal/mole), in most cases, to reported experimental data from NIST. The exception was found with the reactions forming formaldehyde and propene. Due to this, data reported by NIST was included instead.

The Gibbs free energies of reaction were calculated by the following equation:

$$\Delta G = \sum_{products} \nu_i G_i - \sum_{reactants} \nu_j G_j \quad (S2)$$

in which G_i , G_j correspond to Gibbs free energies calculated using Gaussian data and ν_i , ν_j represent stoichiometric values for the given compounds in the chemical reaction of interest.

Another ability inherent in these calculations was to be able to examine sensitivity of ΔG to varying experimental temperatures and pressures. However, trends of ΔG with respect to pressure have been largely omitted from this work. This has been justified due to the negligible change in ΔG in the ranges of pressures feasible to the reaction. Instead, focus has been directed at temperature dependence.

Table S3. Calculated Free Energies of the Dehydra-Decyclization Products of THF using NIST database values. The vapor phase free energies are defined relative to that of THF.

| Temperature (K) | Propene+formaldehyde (Kcal mol ⁻¹) | Butadiene+water (Kcal mol ⁻¹) | 3-buten-1-ol (Kcal mol ⁻¹) |
|--------------------|---|--|---|
| 298 | 8.96 | 0.79 | 7.10 |
| 473 | 1.90 | -5.67 | 6.09 |
| 673 | -6.36 | -13.53 | 4.94 |

Table S4. Calculated Free Energies of the Dehydra-Decyclization Products of THF using the CBS-QB3 method. The vapor phase free energies are defined relative to that of THF.

| Temperature (K) | Propene+formaldehyde (Kcal mol ⁻¹) | Butadiene+water (Kcal mol ⁻¹) | 3-buten-1-ol (Kcal mol ⁻¹) |
|--------------------|---|--|---|
| 298 | 2.917 | 0.832 | 5.642 |
| 473 | -5.057 | -6.735 | 4.238 |
| 673 | -12.263 | -15.666 | 2.392 |

7.0 Catalytic Experimental Results: Dehydra-Decyclization of Tetrahydrofuran (THF)

Table S5. Summarized results for the dehydra-decylization of tetrahydrofuran (THF) to butadiene over P-SPP catalysts using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | |
|---------------------|--------------------------------------|-------------------|-----------------|---------|-----------|---------------------|
| | | | Propene | Butenes | Butadiene | ¹ Others |
| 200 | 88.8 | 0.02 | 0 | 52.78 | 47.22 | 0 |
| 200 | 9.7 | 0.08 | 0 | 9.56 | 83.34 | 7.10 |
| 200 | 0.9 | 0.23 | 0.32 | 3.16 | 96.17 | 0.35 |
| 250 | 88.8 | 0.28 | 0 | 3.62 | 96.38 | 0 |
| 250 | 9.7 | 0.44 | 0.48 | 2.51 | 96.07 | 0.95 |
| 250 | 0.9 | 1.90 | 0.65 | 0.73 | 98.53 | 0.09 |
| 300 | 88.8 | 0.99 | 0 | 2.36 | 97.64 | 0 |
| 300 | 9.7 | 1.83 | 0.61 | 0.96 | 98.16 | 0.26 |
| 300 | 0.9 | 9.11 | 1.08 | 0.20 | 98.56 | 0.17 |
| 350 | 88.8 | 1.84 | 0 | 1.09 | 98.91 | 0 |
| 350 | 9.7 | 4.76 | 0.91 | 0.47 | 98.47 | 0.16 |
| 350 | 0.9 | 30.71 | 1.97 | 0 | 95.79 | 2.23 |
| 400 | 88.8 | 2.81 | 0.84 | 1.30 | 97.20 | 0.66 |
| 400 | 9.7 | 8.93 | 1.58 | 0.36 | 97.40 | 0.65 |
| 400 | 0.9 | 62.85 | 4.55 | 1.26 | 86.29 | 7.90 |
| 400 | 0.6 | 82.99 | 2.52 | 1.39 | 86.09 | 10.01 |
| 400 | 0.2 | 89.11 | 3.29 | 5.11 | 84.65 | 6.94 |

¹Others: Unidentified large molecules

Table S6. Summarized results for the dehydra-decylization of tetrahydrofuran (THF) to butadiene over H-Y catalysts using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | |
|---------------------|--------------------------------------|-------------------|-----------------|---------|-----------|---------------------|
| | | | Propene | Butenes | Butadiene | ¹ Others |
| 200 | 88.8 | 12.73 | 2.14 | 56.31 | 31.07 | 10.48 |
| 200 | 9.7 | 46.55 | 3.87 | 54.95 | 23.51 | 17.67 |
| 200 | 0.9 | 94.64 | 3.35 | 46.82 | 17.76 | 32.07 |
| 250 | 88.8 | 27.90 | 11.77 | 37.85 | 26.22 | 24.16 |
| 250 | 9.7 | 70.00 | 15.21 | 37.98 | 21.80 | 25.01 |
| 250 | 0.9 | 98.01 | 13.46 | 36.63 | 14.09 | 35.82 |
| 300 | 88.8 | 31.71 | 17.35 | 32.88 | 19.62 | 30.15 |
| 300 | 9.7 | 89.30 | 22.34 | 27.66 | 17.36 | 32.64 |
| 300 | 0.9 | 96.69 | 15.88 | 23.15 | 14.26 | 46.71 |
| 350 | 88.8 | 58.16 | 13.81 | 14.92 | 8.56 | 62.70 |
| 350 | 9.7 | 98.03 | 23.75 | 20.55 | 12.29 | 43.42 |
| 350 | 0.9 | 100 | 14.99 | 20.13 | 11.35 | 53.53 |
| 400 | 88.8 | 72.98 | 16.31 | 13.39 | 7.44 | 62.86 |
| 400 | 9.7 | 100 | 22.86 | 17.92 | 8.99 | 50.23 |
| 400 | 0.9 | 100 | 16.00 | 21.45 | 9.57 | 52.98 |

¹Others: Unidentified large molecules

Table S7. Summarized results for the dehydra-decylization of tetrahydrofuran (THF) to butadiene over ZSM-5 catalysts using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | |
|---------------------|--------------------------------------|-------------------|-----------------|---------|-----------|---------------------|
| | | | Propene | Butenes | Butadiene | ¹ Others |
| 200 | 88.8 | 3.04 | 1.78 | 30.21 | 52.61 | 15.40 |
| 200 | 9.7 | 3.33 | 6.43 | 40.79 | 23.32 | 29.46 |
| 200 | 0.9 | 6.57 | 13.99 | 28.66 | 21.87 | 35.47 |
| 250 | 88.8 | 24.03 | 15.14 | 20.65 | 14.18 | 50.02 |
| 250 | 9.7 | 29.81 | 24.86 | 19.68 | 9.79 | 45.66 |
| 250 | 0.9 | 79.56 | 22.89 | 13.55 | 9.12 | 54.45 |
| 300 | 88.8 | 69.51 | 4.90 | 3.09 | 3.55 | 88.46 |
| 300 | 9.7 | 62.95 | 23.68 | 11.06 | 6.92 | 58.34 |
| 300 | 0.9 | 97.68 | 11.90 | 9.65 | 6.24 | 72.20 |
| 350 | 88.8 | 88.06 | 2.52 | 1.36 | 1.58 | 94.54 |
| 350 | 9.7 | 90.65 | 18.07 | 7.79 | 4.37 | 69.77 |
| 350 | 0.9 | 100 | 10.14 | 8.54 | 5.28 | 76.04 |
| 400 | 88.8 | 95.14 | 2.38 | 1.10 | 0.76 | 95.77 |
| 400 | 9.7 | 96.49 | 14.15 | 6.21 | 4.74 | 74.90 |
| 400 | 0.9 | 100 | 10.76 | 8.19 | 4.38 | 76.68 |

¹Others: Unidentified large molecules

Table S8. Summarized results for the dehydra-decylization of tetrahydrofuran (THF) to butadiene over a silica alumina catalyst using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | |
|---------------------|--------------------------------------|-------------------|-----------------|---------|-----------|---------------------|
| | | | Propene | Butenes | Butadiene | ¹ Others |
| 200 | 88.8 | 0.23 | 0.00 | 6.88 | 93.12 | 0 |
| 200 | 9.7 | 1.07 | 0.00 | 3.04 | 95.98 | 0.98 |
| 200 | 0.9 | 1.87 | 1.97 | 2.88 | 94.09 | 1.06 |
| 250 | 88.8 | 2.18 | 0.00 | 2.66 | 92.74 | 4.60 |
| 250 | 9.7 | 9.49 | 19.60 | 2.11 | 68.71 | 9.58 |
| 250 | 0.9 | 18.58 | 19.49 | 0.97 | 70.67 | 8.88 |
| 300 | 88.8 | 18.01 | 11.88 | 0.92 | 74.12 | 13.08 |
| 300 | 9.7 | 53.66 | 34.07 | 1.42 | 52.41 | 12.09 |
| 300 | 0.9 | 92.89 | 33.18 | 1.86 | 53.74 | 11.22 |
| 350 | 88.8 | 44.05 | 26.28 | 1.67 | 50.17 | 21.88 |
| 350 | 9.7 | 77.78 | 48.38 | 1.21 | 40.72 | 9.69 |
| 350 | 0.9 | 100 | 49.67 | 3.16 | 33.68 | 13.49 |
| 400 | 88.8 | 58.17 | 27.61 | 0.89 | 23.40 | 48.11 |
| 400 | 9.7 | 85.84 | 48.98 | 2.08 | 35.50 | 13.44 |
| 400 | 0.9 | 100 | 52.44 | 0.32 | 24.20 | 23.05 |

¹Others: Unidentified large molecules

Table S9. Summarized results for the dehydra-decylization of tetrahydrofuran (THF) to butadiene over Nb₂O₅ catalysts using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | |
|---------------------|--------------------------------------|-------------------|-----------------|---------|-----------|---------------------|
| | | | Propene | Butenes | Butadiene | ¹ Others |
| 200 | 88.8 | 0.01 | 0 | 44.10 | 55.90 | 0 |
| 200 | 9.7 | 0.02 | 0.00 | 27.43 | 39.45 | 33.12 |
| 200 | 0.9 | 0.01 | 5.43 | 34.03 | 47.59 | 12.95 |
| 250 | 88.8 | 0.21 | 0 | 3.11 | 90.36 | 6.53 |
| 250 | 9.7 | 0.20 | 3.64 | 4.78 | 83.46 | 8.12 |
| 250 | 0.9 | 0.14 | 3.69 | 5.42 | 64.92 | 25.97 |
| 300 | 88.8 | 1.02 | 8.65 | 1.47 | 87.78 | 2.10 |
| 300 | 9.7 | 0.94 | 20.92 | 0.91 | 73.41 | 4.75 |
| 300 | 0.9 | 1.33 | 19.57 | 5.70 | 64.04 | 10.70 |
| 350 | 88.8 | 0.91 | 21.36 | 1.19 | 72.82 | 4.63 |
| 350 | 9.7 | 1.36 | 22.04 | 1.51 | 64.14 | 12.30 |
| 350 | 0.9 | 6.89 | 23.89 | 7.43 | 57.08 | 11.59 |
| 400 | 88.8 | 1.12 | 19.06 | 10.40 | 64.28 | 6.27 |
| 400 | 9.7 | 2.05 | 17.60 | 10.48 | 54.94 | 16.97 |
| 400 | 0.9 | 27.43 | 26.83 | 11.85 | 47.76 | 13.56 |

¹Others: Unidentified large molecules

Table S10. Summarized results for the dehydra-decylization of tetrahydrofuran (THF) to butadiene over Sn-BEA catalysts using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | |
|---|--------------------------------------|-------------------|-----------------|---------|-----------|---------------------|
| | | | Propene | Butenes | Butadiene | ¹ Others |
| 200 | 88.8 | 0.02 | 17 | 38 | 44.93 | 0 |
| 200 | 9.7 | 0.05 | 3.97 | 15 | 78.95 | 2.25 |
| 300 | 88.8 | 0.11 | 12.61 | 16 | 64.37 | 7.39 |
| 300 | 9.7 | 0.63 | 15.67 | 5 | 59.56 | 19.71 |
| 400 | 88.8 | 0.60 | 30.26 | 6 | 50.30 | 13.04 |
| 400 | 9.7 | 3.39 | 31.66 | 4.77 | 44.42 | 19.16 |
| ¹ Others: Unidentified large molecules | | | | | | |

Table S11. Summarized results for the dehydra-decylization of tetrahydrofuran (THF) to butadiene over ZrO₂ catalysts using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | |
|---|--------------------------------------|-------------------|-----------------|---------|-----------|---------------------|
| | | | Propene | Butenes | Butadiene | ¹ Others |
| 200 | 88.8 | 0.01 | 22.54 | 39.44 | 38.03 | 0 |
| 200 | 9.7 | 0.01 | 2.94 | 38.17 | 46.11 | 12.78 |
| 300 | 88.8 | 0.90 | 17.64 | 1.17 | 78.20 | 2.99 |
| 300 | 9.7 | 2.02 | 20.49 | 1.17 | 72.35 | 5.99 |
| 400 | 88.8 | 2.14 | 31.73 | 7.99 | 52.52 | 7.76 |
| 400 | 9.7 | 5.04 | 30.70 | 3.09 | 54.96 | 11.25 |
| ¹ Others: Unidentified large molecules | | | | | | |

Table S12. Summarized results for the dehydra-decylization of tetrahydrofuran (THF) to butadiene over phosphotungstic acid (PWA) catalysts using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | |
|---|--------------------------------------|-------------------|-----------------|---------|-----------|---------------------|
| | | | Propene | Butenes | Butadiene | ¹ Others |
| 200 | 88.8 | 0.81 | 8.78 | 22.57 | 63.17 | 5.48 |
| 200 | 9.7 | 1.92 | 8.59 | 32.66 | 44.92 | 13.83 |
| 300 | 88.8 | 4.45 | 10.08 | 20.49 | 48.98 | 20.45 |
| 300 | 9.7 | 8.96 | 11.98 | 25.48 | 29.17 | 33.37 |
| 400 | 88.8 | 24.87 | 5.86 | 2.45 | 26.91 | 64.78 |
| 400 | 9.7 | 29.82 | 8.52 | 3.34 | 31.39 | 56.76 |
| ¹ Others: Unidentified large molecules | | | | | | |

Table S13. Summarized results for the dehydra-decylization of tetrahydrofuran (THF) to butadiene over P-MFI catalysts using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | |
|---------------------|--------------------------------------|-------------------|-----------------|---------|-----------|---------------------|
| | | | Propene | Butenes | Butadiene | ¹ Others |
| 200 | 133.2 | 0.03 | 19.25 | 20.83 | 59.92 | 0.00 |
| 200 | 14.5 | 0.30 | 0.99 | 2.53 | 95.07 | 1.40 |
| 200 | 1.3 | 0.38 | 0.49 | 5.47 | 92.89 | 1.15 |
| 250 | 133.2 | 0.47 | 1.22 | 1.98 | 96.35 | 0.46 |
| 250 | 14.5 | 0.87 | 0.86 | 1.47 | 97.05 | 0.62 |
| 250 | 1.3 | 3.16 | 1.07 | 0.48 | 97.83 | 0.62 |
| 300 | 133.2 | 0.68 | 1.93 | 0.98 | 95.90 | 1.19 |
| 300 | 14.5 | 3.96 | 1.58 | 0.41 | 97.64 | 0.37 |
| 300 | 1.3 | 16.76 | 1.50 | 1.15 | 95.49 | 1.86 |
| 350 | 133.2 | 1.70 | 1.80 | 4.66 | 91.92 | 1.61 |
| 350 | 14.5 | 5.87 | 2.23 | 2.23 | 94.01 | 1.53 |
| 350 | 1.3 | 44.18 | 2.32 | 0.59 | 92.02 | 5.07 |
| 400 | 133.2 | 2.33 | 3.37 | 3.68 | 90.90 | 2.05 |
| 400 | 14.5 | 8.54 | 3.36 | 2.01 | 92.45 | 2.18 |
| 400 | 1.3 | 68.32 | 3.09 | 0.48 | 85.98 | 10.45 |
| 400 | 1.0 | 81.84 | 2.97 | 0.47 | 82.75 | 13.81 |
| 400 | 0.4 | 95.21 | 3.35 | 3.30 | 79.69 | 13.66 |

¹Others: Unidentified large molecules

Table S14. Summarized results for the dehydra-decylization of tetrahydrofuran (THF) to butadiene over P-BEA catalysts using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | |
|---------------------|--------------------------------------|-------------------|-----------------|---------|-----------|---------------------|
| | | | Propene | Butenes | Butadiene | ¹ Others |
| 200 | 88.8 | 0.06 | 0.00 | 24.90 | 75.10 | 0.00 |
| 200 | 9.7 | 0.19 | 0.64 | 4.59 | 94.61 | 0.16 |
| 200 | 0.9 | 0.48 | 0.54 | 2.41 | 96.82 | 0.22 |
| 250 | 88.8 | 0.26 | 0.00 | 3.80 | 96.20 | 0.00 |
| 250 | 9.7 | 0.66 | 6.70 | 2.24 | 91.02 | 0.04 |
| 250 | 0.9 | 2.29 | 1.97 | 1.62 | 96.36 | 0.04 |
| 300 | 88.8 | 0.73 | 2.93 | 3.11 | 93.96 | 0.00 |
| 300 | 9.7 | 1.95 | 8.48 | 1.23 | 90.24 | 0.05 |
| 300 | 0.9 | 9.12 | 7.22 | 1.55 | 85.04 | 6.19 |
| 350 | 88.8 | 1.41 | 4.52 | 1.85 | 93.64 | 0.00 |
| 350 | 9.7 | 4.67 | 9.65 | 0.88 | 87.03 | 2.45 |
| 350 | 0.9 | 24.45 | 7.27 | 1.63 | 83.63 | 7.47 |
| 400 | 88.8 | 2.10 | 9.59 | 1.26 | 89.15 | 0.00 |
| 400 | 9.7 | 8.56 | 11.17 | 0.88 | 84.73 | 3.22 |
| 400 | 0.9 | 46.13 | 8.40 | 1.28 | 78.99 | 11.32 |
| 400 | 0.6 | 76.48 | 8.79 | 0.53 | 67.40 | 23.28 |
| 400 | 0.2 | 85.85 | 8.37 | 0.55 | 61.55 | 29.54 |

¹Others: Unidentified large molecules

Table S15. Summarized results for the dehydra-decylization of tetrahydrofuran (THF) to butadiene over P-Al-BEA catalysts using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | |
|---|--------------------------------------|-------------------|-----------------|---------|-----------|---------------------|
| | | | Propene | Butenes | Butadiene | ¹ Others |
| 200 | 88.8 | 19.09 | 0 | 57.66 | 36.96 | 5.38 |
| 200 | 9.7 | 100 | 14.44 | 22.52 | 16.65 | 46.39 |
| 200 | 0.9 | 100 | 3.86 | 44.36 | 6.58 | 45.20 |
| 210 | 88.8 | 28.68 | 23.30 | 45.42 | 22.10 | 9.18 |
| 220 | 88.8 | 34.83 | 21.21 | 41.18 | 19.55 | 18.07 |
| 230 | 88.8 | 45.05 | 26.13 | 32.02 | 13.65 | 28.20 |
| 250 | 88.8 | 63.68 | 12.60 | 22.24 | 9.59 | 55.57 |
| 250 | 9.7 | 100 | 21.15 | 26.56 | 5.02 | 47.27 |
| 250 | 0.9 | 100 | 7.98 | 35.70 | 8.11 | 48.21 |
| 300 | 88.8 | 74.12 | 17.82 | 18.91 | 5.98 | 57.28 |
| 300 | 9.7 | 100 | 17.64 | 28.92 | 3.56 | 49.88 |
| 300 | 0.9 | 100 | 10.01 | 41.61 | 7.31 | 41.07 |
| 350 | 88.8 | 79.47 | 21.04 | 14.68 | 4.86 | 59.42 |
| 350 | 9.7 | 100 | 16.47 | 28.52 | 3.73 | 51.28 |
| 350 | 0.9 | 100 | 12.41 | 43.68 | 7.17 | 36.74 |
| 400 | 88.8 | 88.57 | 17.47 | 10.14 | 3.37 | 69.02 |
| 400 | 9.7 | 100 | 16.51 | 25.58 | 4.24 | 53.67 |
| 400 | 0.9 | 100 | 16.81 | 34.27 | 8.42 | 40.49 |
| ¹ Others: Unidentified large molecules | | | | | | |

Table S16. Summarized results for the dehydra-decylization of tetrahydrofuran (THF) to butadiene over Na₃PO₄ catalysts using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | |
|---------------------|--------------------------------------|-------------------|-----------------|---------|-----------|---------------------|
| | | | Propene | Butenes | Butadiene | ¹ Others |
| 200 | 88.8 | 0 | 0 | 0 | 0 | 0 |
| 200 | 9.7 | 0.002 | 21.519 | 0 | 15.190 | 63.291 |
| 200 | 0.9 | 0.001 | 5.200 | 6.800 | 24.400 | 63.600 |
| 250 | 88.8 | 0.004 | 100 | 0 | 0 | 0 |
| 250 | 9.7 | 0.002 | 24.000 | 0 | 16.000 | 60.000 |
| 250 | 0.9 | 0.002 | 5.139 | 8.672 | 23.126 | 63.062 |
| 300 | 88.8 | 0.008 | 100 | 0 | 0 | 0 |
| 300 | 9.7 | 0.002 | 22.472 | 0.000 | 19.101 | 58.427 |
| 300 | 0.9 | 0.008 | 16.983 | 10.964 | 10.002 | 62.051 |
| 350 | 88.8 | 0.005 | 100 | 0 | 0 | 0 |
| 350 | 9.7 | 0.085 | 40.464 | 2.092 | 8.745 | 48.700 |
| 350 | 0.9 | 0.105 | 36.004 | 4.074 | 8.001 | 51.921 |
| 400 | 88.8 | 0.009 | 27.273 | 0 | 25.000 | 47.727 |
| 400 | 9.7 | 0.120 | 31.777 | 1.674 | 11.783 | 54.766 |
| 400 | 0.9 | 0.087 | 25.942 | 8.980 | 7.924 | 57.154 |

¹Others: Unidentified large molecules

Table S17. Packed bed reactor summary of THF dehydra-decyclization to butadiene over P-SPP. THF partial pressure was held constant at 4.9 torr.

| Temperature (°C) | WHSV (g THF g cat ⁻¹ hr ⁻¹) | Conversion (%) | Selectivity (%) | | | | Carbon balance (%) |
|---------------------|--|-------------------|-----------------|-----------|---------|--------|--------------------------|
| | | | Propene | Butadiene | Butenes | Others | |
| 250 | 0.99 | 0.3 | 0.0 | 97.9 | 2.1 | 0.0 | 97.3 |
| 275 | 0.99 | 0.9 | 1.2 | 96.6 | 1.2 | 1.0 | 91.6 |
| 300 | 0.99 | 2.1 | 1.4 | 96.7 | 1.0 | 1.0 | 104.6 |
| 325 | 0.99 | 4.2 | 1.7 | 96.4 | 1.3 | 0.6 | 102.8 |
| 350 | 0.99 | 6.9 | 2.0 | 96.4 | 1.1 | 0.5 | 100.6 |
| 350 | 0.32 | 17.5 | 2.3 | 94.8 | 1.2 | 1.6 | 92.0 |
| 350 | 0.10 | 37.4 | 2.4 | 93.0 | 2.6 | 2.0 | 108.3 |
| 350 | 0.04 | 53.5 | 1.8 | 91.7 | 1.8 | 4.7 | 102.8 |
| 375 | 0.10 | 45.0 | 3.2 | 91.5 | 3.0 | 2.3 | 102.3 |
| 375 | 0.04 | 78.0 | 2.5 | 88.5 | 3.6 | 5.5 | 104.4 |
| 400 | 0.04 | 82.9 | 2.9 | 87.4 | 3.7 | 6.1 | 97.2 |

Table S18. Packed bed reactor summary of THF dehydra-decyclization to butadiene over ZSM-5. THF partial pressure was held constant at 4.9 torr.

| Temperature (°C) | WHSV (g THF g cat ⁻¹ hr ⁻¹) | Conversion (%) | Selectivity (%) | | | | Carbon balance (%) |
|---------------------|--|-------------------|-----------------|-----------|---------|--------|--------------------------|
| | | | Propene | Butadiene | Butenes | Others | |
| 250 | 1.00 | 4.3 | 16.8 | 41.3 | 24.5 | 17.4 | 100.6 |
| 275 | 1.00 | 7.8 | 14.4 | 38.9 | 17.9 | 28.7 | 97.7 |
| 300 | 1.00 | 13.7 | 13.6 | 34.7 | 17.0 | 34.7 | 98.2 |
| 325 | 1.00 | 18.2 | 13.7 | 33.7 | 15.3 | 37.3 | 88.3 |
| 350 | 1.00 | 19.7 | 14.2 | 35.1 | 12.7 | 38.1 | 97.1 |

Table S19. Packed bed reactor summary of THF dehydra-decyclization to butadiene over Sn-BEA. THF partial pressure was held constant at 4.9 torr.

| Temperature (°C) | WHSV (g THF g cat ⁻¹ hr ⁻¹) | Conversion (%) | Selectivity (%) | | | | Carbon balance (%) |
|---------------------|--|-------------------|-----------------|-----------|---------|--------|--------------------------|
| | | | Propene | Butadiene | Butenes | Others | |
| 250 | 1.00 | 1.0 | 10.7 | 73.3 | 15.2 | 0.8 | 102.8 |
| 275 | 1.00 | 1.4 | 13.9 | 66.0 | 12.9 | 7.2 | 99.7 |
| 300 | 1.00 | 2.4 | 17.7 | 60.1 | 11.4 | 10.8 | 95.3 |
| 325 | 1.00 | 4.2 | 22.0 | 52.5 | 9.9 | 15.5 | 96.2 |
| 350 | 1.00 | 6.0 | 28.4 | 46.8 | 7.3 | 17.6 | 98.4 |

Table S20. Packed bed reactor summary of THF dehydra-decyclization to butadiene over silica alumina. THF partial pressure was held constant at 4.9 torr.

| Temperature (°C) | WHSV (g THF g cat ⁻¹ hr ⁻¹) | Conversion (%) | Selectivity (%) | | | | Carbon balance (%) |
|---------------------|--|-------------------|-----------------|-----------|---------|--------|--------------------------|
| | | | Propene | Butadiene | Butenes | Others | |
| 250 | 1.01 | 0.6 | 37.4 | 53.4 | 9.2 | 0.0 | 101.7 |
| 275 | 1.01 | 1.8 | 42.7 | 46.9 | 4.8 | 5.6 | 101.8 |
| 300 | 1.01 | 4.8 | 46.2 | 47.1 | 2.3 | 4.4 | 107.4 |
| 325 | 1.01 | 11.4 | 48.1 | 45.5 | 2.7 | 3.7 | 95.2 |
| 350 | 1.01 | 22.4 | 50.1 | 43.1 | 3.0 | 3.9 | 94.1 |

8.0 Catalytic Experimental Results: Dehydra-Decyclization of 2-methyltetrahydrofuran (2-MTHF)

Table S21. Summarized results for the dehydra-decylization of 2-methyltetrahydrofuran (2-MTHF) to pentadienes over P-SPP catalysts using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | | |
|---------------------|---|-------------------|-----------------|---------|------------|--------------------|--------------------|
| | | | Propene | Butenes | Pentadiene | | |
| | | | | | Isoprene | 1,4- pentadiene | 1,3- pentadiene |
| 200 | 88.8 | 0.33 | 0.00 | 5.60 | 1.11 | 13.16 | 75.83 |
| 200 | 9.7 | 1.62 | 0.02 | 1.71 | 0.57 | 12.49 | 82.15 |
| 200 | 0.9 | 5.26 | 0.01 | 0.81 | 2.52 | 12.55 | 82.29 |
| 250 | 88.8 | 2.98 | 0.00 | 1.26 | 1.30 | 14.50 | 82.06 |
| 250 | 9.7 | 7.79 | 0.10 | 0.90 | 0.49 | 13.69 | 82.27 |
| 250 | 0.9 | 34.06 | 0.21 | 1.22 | 5.07 | 10.76 | 75.74 |
| 300 | 88.8 | 3.36 | 0.06 | 1.58 | 1.92 | 15.97 | 77.43 |
| 300 | 9.7 | 16.50 | 0.16 | 1.05 | 1.48 | 14.36 | 79.05 |
| 300 | 0.9 | 74.10 | 0.92 | 2.65 | 2.16 | 8.25 | 59.80 |
| 350 | 88.8 | 3.67 | 0.12 | 2.47 | 1.01 | 17.53 | 70.79 |
| 350 | 9.7 | 31.91 | 0.28 | 1.39 | 2.02 | 14.69 | 76.26 |
| 350 | 0.9 | 94.55 | 1.89 | 4.45 | 3.77 | 7.48 | 42.90 |
| 400 | 88.8 | 4.53 | 0.20 | 2.74 | 0.98 | 20.06 | 67.66 |
| 400 | 9.7 | 46.25 | 0.34 | 1.75 | 1.92 | 14.36 | 74.94 |
| 400 | 0.9 | 99.15 | 2.55 | 5.44 | 3.44 | 5.99 | 37.83 |

Table S22. Packed bed reactor summary of 2-methyltetrahydrofuran (2-MTHF) dehydrocyclization to pentadienes over P-SPP. 2-MTHF partial pressure was held constant at 4.9 torr.

| Temperature (°C) | WHSV (g 2-MTHF g cat ⁻¹ hr ⁻¹) | Conversion (%) | Selectivity (%) | | | | | Carbon Balance (%) |
|---------------------|---|-------------------|-----------------|---------|-------------|------|-----------|--------------------------|
| | | | Propene | Butenes | Pentadienes | | | |
| | | | | | Isoprene | 1,4 | 1,3 (E,Z) | |
| 250 | 1.00 | 4.1 | 0.0 | 1.5 | 3.6 | 18.3 | 76.4 | 99.2 |
| 275 | 1.00 | 8.5 | 0.0 | 1.1 | 3.9 | 19.2 | 75.6 | 92.1 |
| 300 | 1.00 | 14.6 | 0.1 | 1.0 | 3.7 | 19.3 | 75.6 | 98.6 |
| 325 | 1.00 | 22.7 | 0.1 | 1.3 | 3.7 | 18.7 | 75.9 | 99.6 |
| 350 | 1.00 | 32.5 | 0.1 | 1.6 | 3.6 | 18.1 | 76.3 | 97.6 |

Table S23. Packed bed reactor summary of 2-methyltetrahydrofuran (2-MTHF) dehydrocyclization to pentadienes over silica alumina. 2-MTHF partial pressure was held constant at 4.9 torr.

| Temperature (°C) | WHSV (g 2-MTHF g cat ⁻¹ hr ⁻¹) | Conversion (%) | Selectivity (%) | | | | | Carbon Balance (%) |
|---------------------|---|-------------------|-----------------|---------|-------------|------|-----------|--------------------------|
| | | | Propene | Butenes | Pentadienes | | | |
| | | | | | Isoprene | 1,4 | 1,3 (E,Z) | |
| 250 | 1.00 | 19.6 | 1.8 | 15.5 | 13.0 | 20.9 | 42.2 | 94.3 |
| 275 | 1.00 | 30.7 | 1.8 | 19.2 | 11.6 | 19.4 | 39.0 | 98.2 |
| 300 | 1.00 | 54.8 | 1.9 | 22.0 | 6.5 | 19.9 | 39.7 | 95.2 |
| 325 | 1.00 | 78.5 | 1.8 | 24.1 | 3.4 | 18.6 | 41.5 | 93.5 |
| 350 | 1.00 | 95.6 | 1.8 | 26.1 | 2.4 | 13.7 | 46.1 | 89.9 |

9.0 Catalytic Experimental Results: Dehydra-Decyclization of 2,5-dimethyltetrahydrofuran (2,5-DMTHF)

Table S24. Summarized results for the dehydra-decylization of 2,5-dimethyltetrahydrofuran (2,5-DMTHF) to hexadienes over P-SPP catalysts using the microcatalytic method.

| Temperature (°C) | Space velocity (s ⁻¹) | Conversion (%) | Selectivity (%) | | | |
|---------------------|---|-------------------|-----------------|---------|-----------------------------|-------------------------|
| | | | Propene | Butenes | ¹ C ₅ | ² Hexadienes |
| 200 | 88.8 | 5.62 | 0.08 | 0.60 | 0.06 | 90.23 |
| 200 | 9.7 | 22.80 | 0.05 | 0.53 | 0.16 | 90.43 |
| 200 | 0.9 | 62.41 | 0.00 | 0.73 | 0.59 | 88.67 |
| 250 | 88.8 | 10.32 | 0.04 | 1.61 | 1.58 | 81.23 |
| 250 | 9.7 | 37.95 | 0.11 | 0.88 | 0.37 | 84.12 |
| 250 | 0.9 | 89.45 | 0.60 | 2.40 | 2.07 | 74.04 |
| 300 | 88.8 | 15.04 | 0.07 | 1.54 | 1.01 | 85.51 |
| 300 | 9.7 | 59.94 | 0.20 | 1.31 | 0.53 | 82.92 |
| 300 | 0.9 | 97.32 | 1.89 | 6.13 | 4.81 | 62.72 |
| 350 | 88.8 | 22.58 | 0.11 | 1.66 | 0.75 | 83.91 |
| 350 | 9.7 | 78.33 | 0.30 | 1.85 | 0.67 | 80.81 |
| 350 | 0.9 | 100 | 2.67 | 7.67 | 6.00 | 59.82 |
| 400 | 88.8 | 30.77 | 0.14 | 1.92 | 0.42 | 82.85 |
| 400 | 9.7 | 88.05 | 0.38 | 2.30 | 0.65 | 77.87 |
| 400 | 0.9 | 100 | 3.19 | 8.58 | 6.26 | 56.65 |

¹C₅: Isoprene and (1,3- and 1,4-) Pentadienes

²1,3-Hexadiene, 1,4-Hexadiene (E,Z), 1,5-Hexadiene and 2,4 Hexadiene (EE,ZZ,EZ)

Table S25. Packed bed reactor summary of 2,5-dimethyltetrahydrofuran (2,5-DMTHF) dehydrocyclization to pentadienes over P-SPP. 2,5-DMTHF partial pressure was held constant at 4.9 torr.

| Temperature (°C) | WHSV (g 2,5-DMTHF g cat ⁻¹ hr ⁻¹) | Conversion (%) | Selectivity (%) | | | | Carbon Balance (%) |
|---------------------|--|-------------------|-----------------|---------|-----------------------------|-------------------------|--------------------------|
| | | | Propene | Butenes | ¹ C ₅ | ² Hexadienes | |
| 250 | 1.00 | 8.7 | 0.0 | 0.8 | 1.8 | 97.3 | 96.7 |
| 275 | 1.00 | 17.1 | 0.1 | 0.7 | 1.2 | 98.0 | 100.9 |
| 300 | 1.00 | 27.3 | 0.1 | 0.9 | 0.5 | 98.5 | 103.2 |
| 325 | 1.00 | 38.0 | 0.1 | 1.0 | 0.5 | 98.4 | 100.2 |
| 350 | 1.00 | 48.7 | 0.1 | 1.3 | 0.7 | 98.0 | 94.7 |

¹C₅: Isoprene and (1,3- and 1,4-) Pentadienes

²1,3-Hexadiene, 1,4-Hexadiene (E,Z), 1,5-Hexadiene and 2,4 Hexadiene (EE,ZZ,EZ)

10.0 Catalytic Experimental Results: Isopropanol dehydration

To assess the performance of the packed bed reactor, the dehydration reaction of isopropanol (IPA) to propene was examined over the silica alumina catalyst. Typically, alcohol dehydration reactions exhibit a near zero order dependence in alcohol partial pressure and an apparent activation barrier of approximately 100 kJ mol⁻¹ under kinetic control [37,38]. At 398 K, the reaction order in IPA was measured to be 0.18 ± 0.03 with an apparent barrier of 92.3 ± 11.4 kJ.mol⁻¹ measured at a IPA partial pressure of 42 torr. Uncertainty in kinetic measurements are reported at a 95% confidence level.

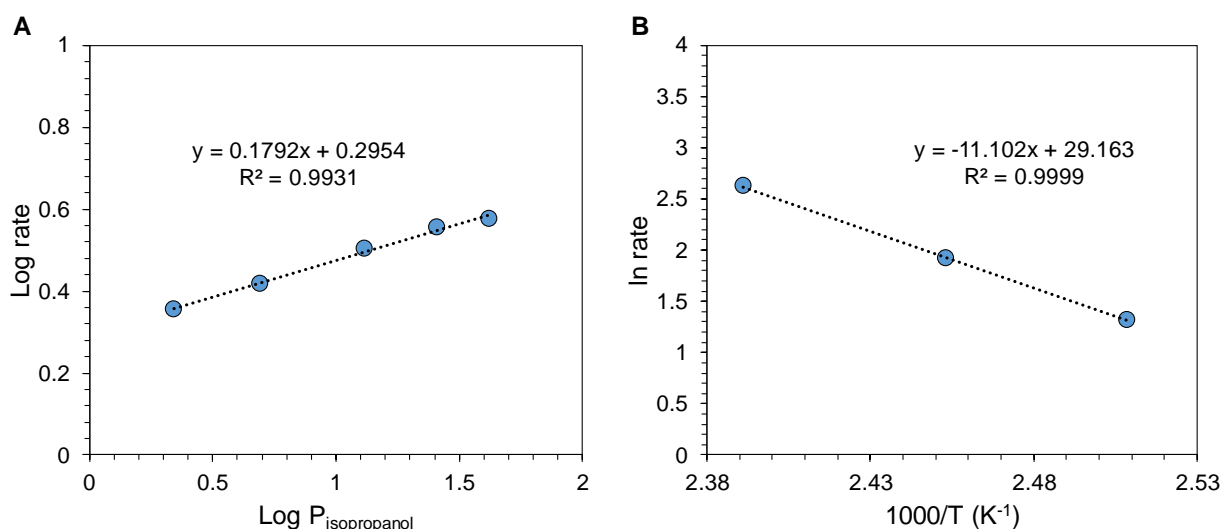


Figure S3. Kinetic measurements of isopropanol dehydration over a silica-alumina catalyst. **A** The effect of isopropanol partial pressure on the rate of dehydration to propene at 398 K between 2.2 and 42 torr of isopropanol. **B** The effect of temperature on the rate of isopropanol dehydration to propene at a fixed isopropanol partial pressure of 42 torr. Conversions were maintained below 2%.

11.0 Product identification: Mass Spectrum Fragmentation Patterns

Verification of the identity of product chemical compounds was conducted through the injection of standards and comparison with retention times by gas chromatography. In addition, the microcatalytic method was coupled with a gas chromatography system with a mass spectrometer detector. In a manner identical to which the microcatalytic method was implemented (Section S5), a quartz tube packed with catalyst was placed in the liner of a GC equipped with a mass spectrometer detector. In the case of tetrahydrofuran, across all catalysts tested, butadiene was the only diolefin detected. During the dehydra-decyclization of 2-MTHF, the formation of 1,4-pentadiene, 1,3-pentadiene (E,Z) and isoprene was detected. In the case of 2,5-DMTHF, eight various hexadiene isomers were detected including: 1,3-hexadiene (E,Z), 1,4-hexadiene (E,Z), 1,5-hexadiene and 2,4-hexadiene (EE,ZZ,EZ). Shown in Figures S4-S13 are the mass spectrum fragmentation patterns of the various products detected in the course of applying the microcatalytic method to a P-SPP catalyst with THF, 2-MTHF and 2,5-DMTHF as the injected reactant.

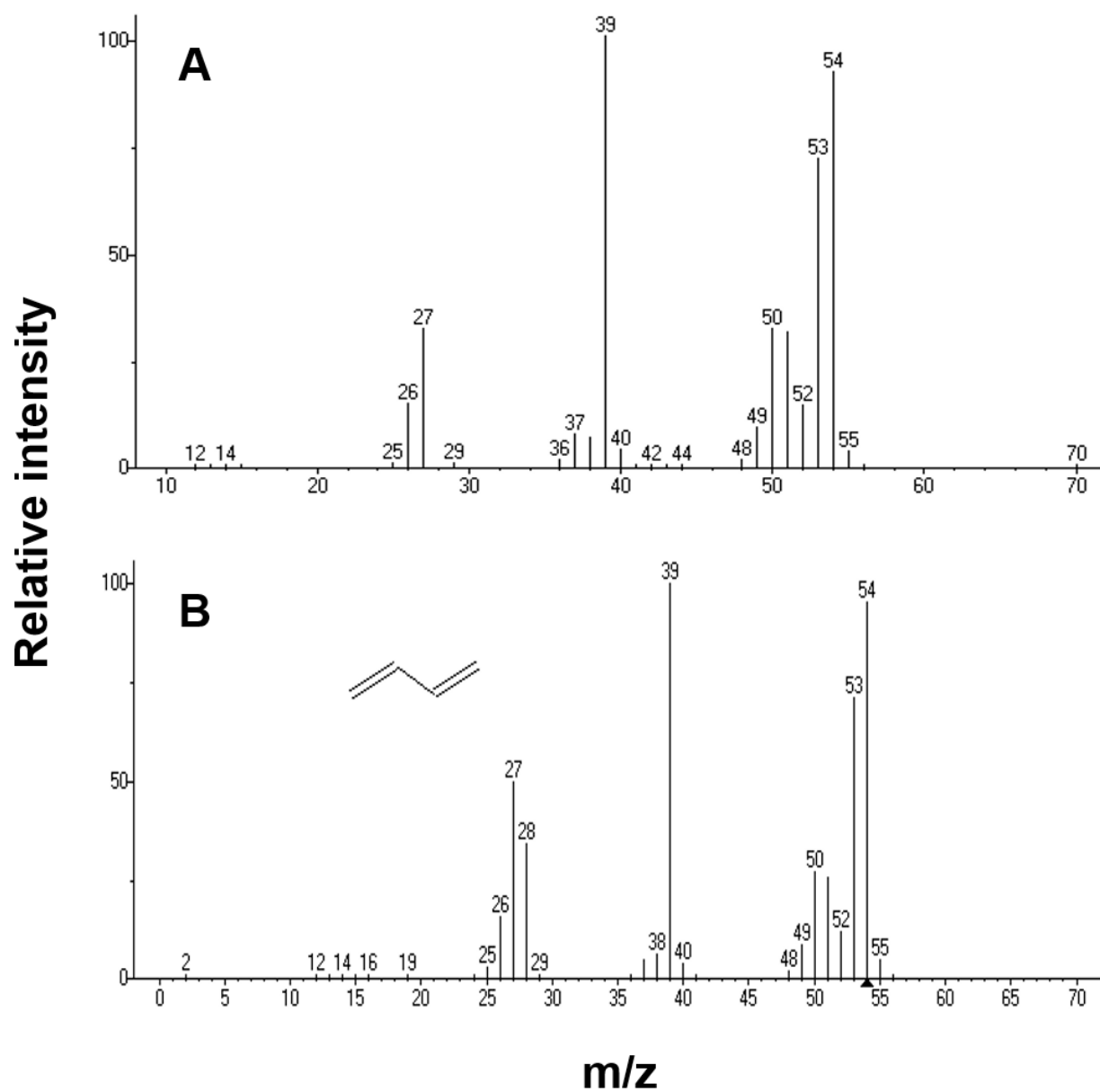


Figure S4. Mass spectrum fragmentation pattern of butadiene **A** produced over P-SPP from THF using the microcatalytic method at 400 °C **B** NIST mass spectrum fragmentation pattern library.

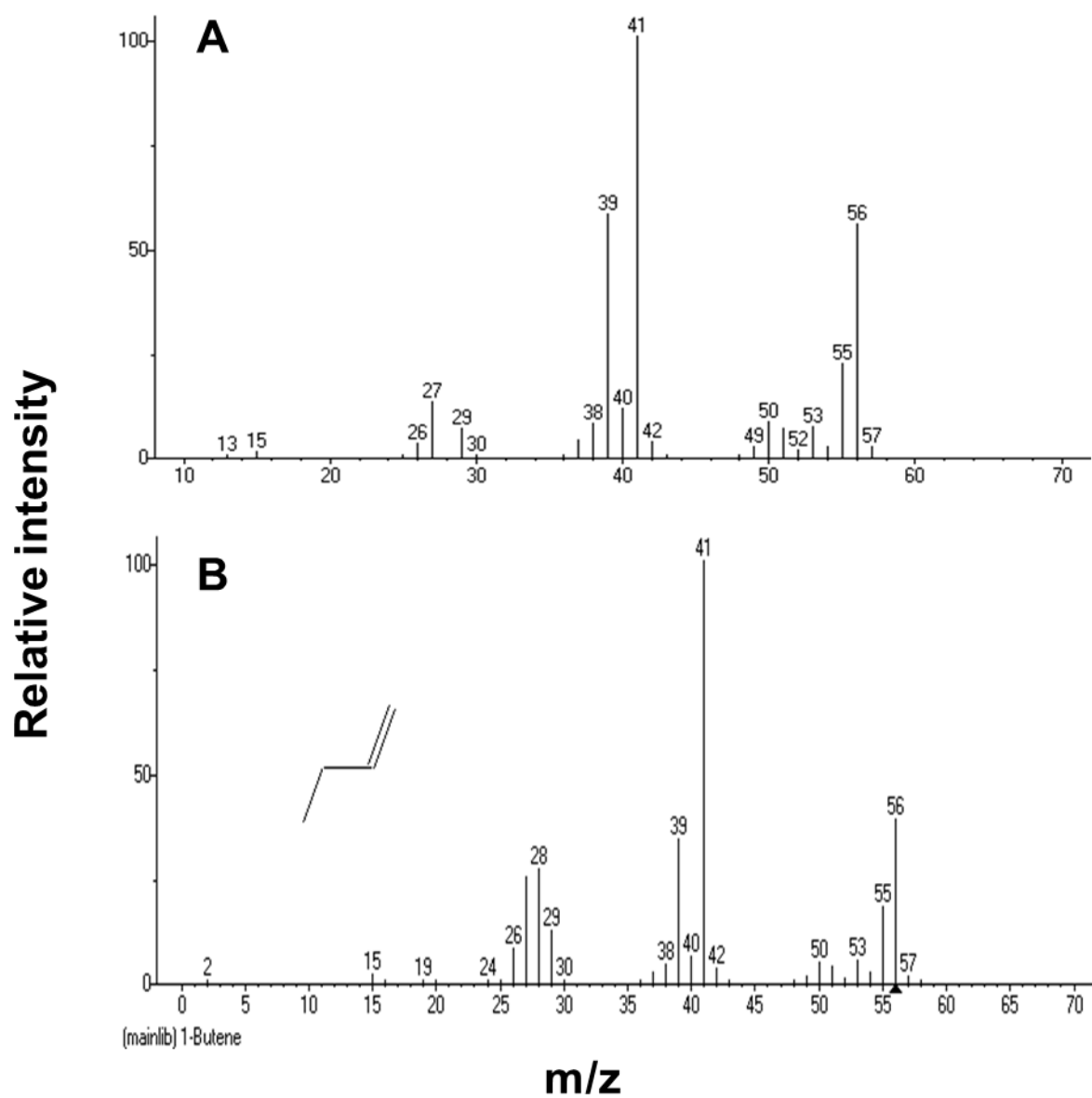


Figure S5. Mass spectrum fragmentation pattern of butene **A** produced over P-SPP from THF using the microcatalytic method at 400 °C **B** NIST mass spectrum fragmentation pattern library.

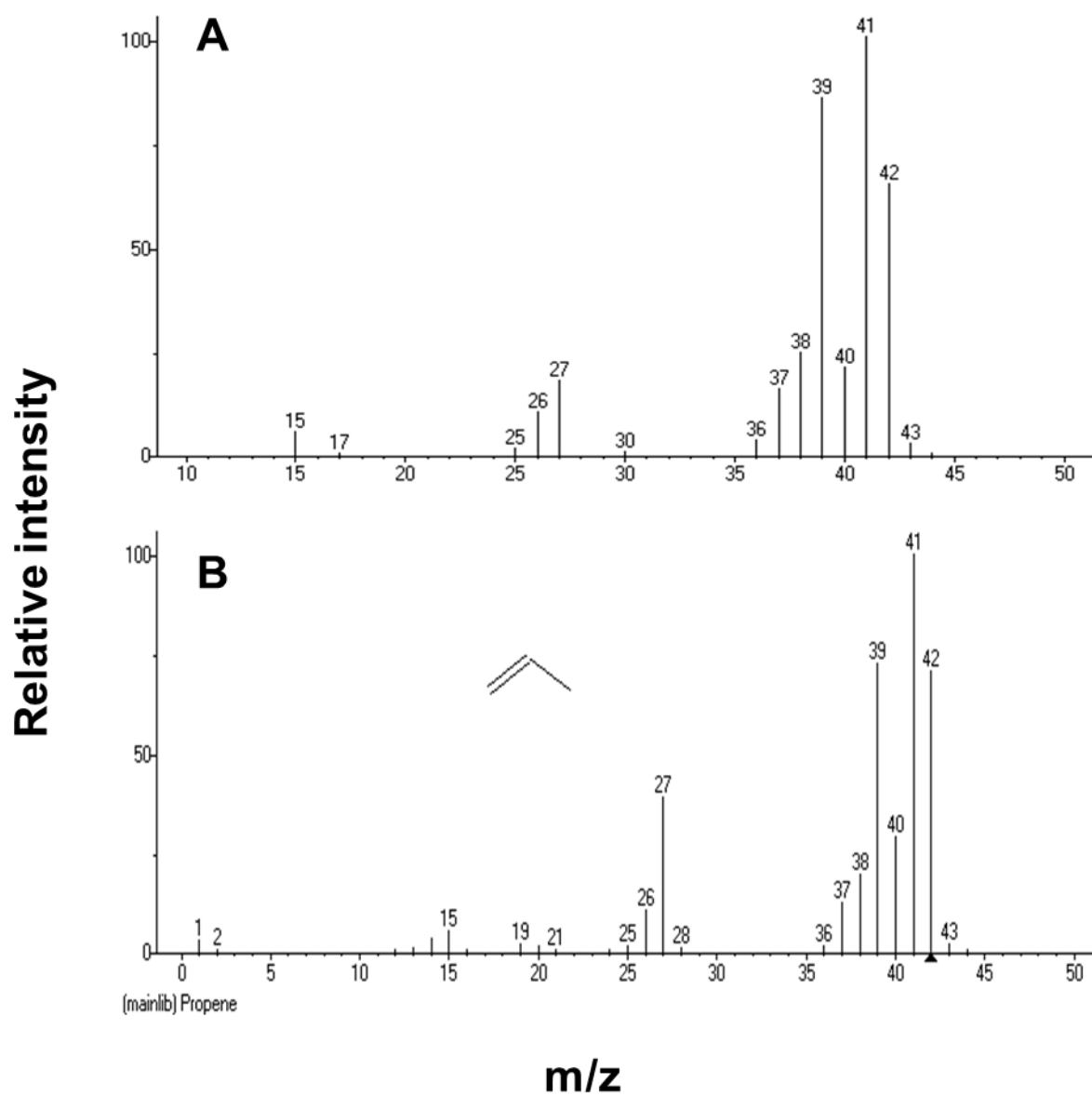


Figure S6. Mass spectrum fragmentation pattern of propene **A** produced over P-SPP from THF using the microcatalytic method at 400 °C **B** NIST mass spectrum fragmentation pattern library.

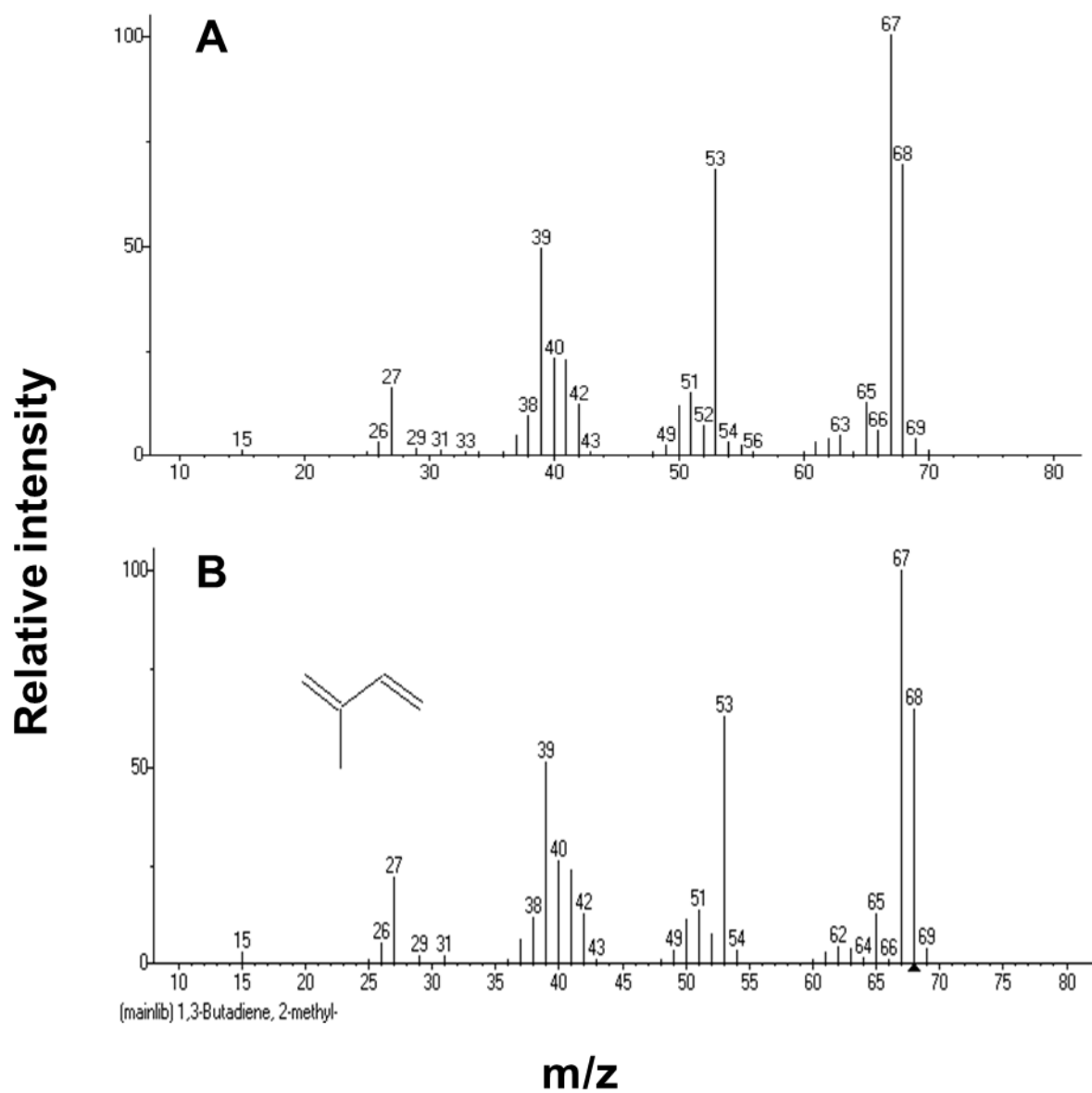


Figure S7. Mass spectrum fragmentation pattern of isoprene **A** produced over P-SPP from 2-MTHF using the microcatalytic method at 400 °C **B** NIST mass spectrum fragmentation pattern library.

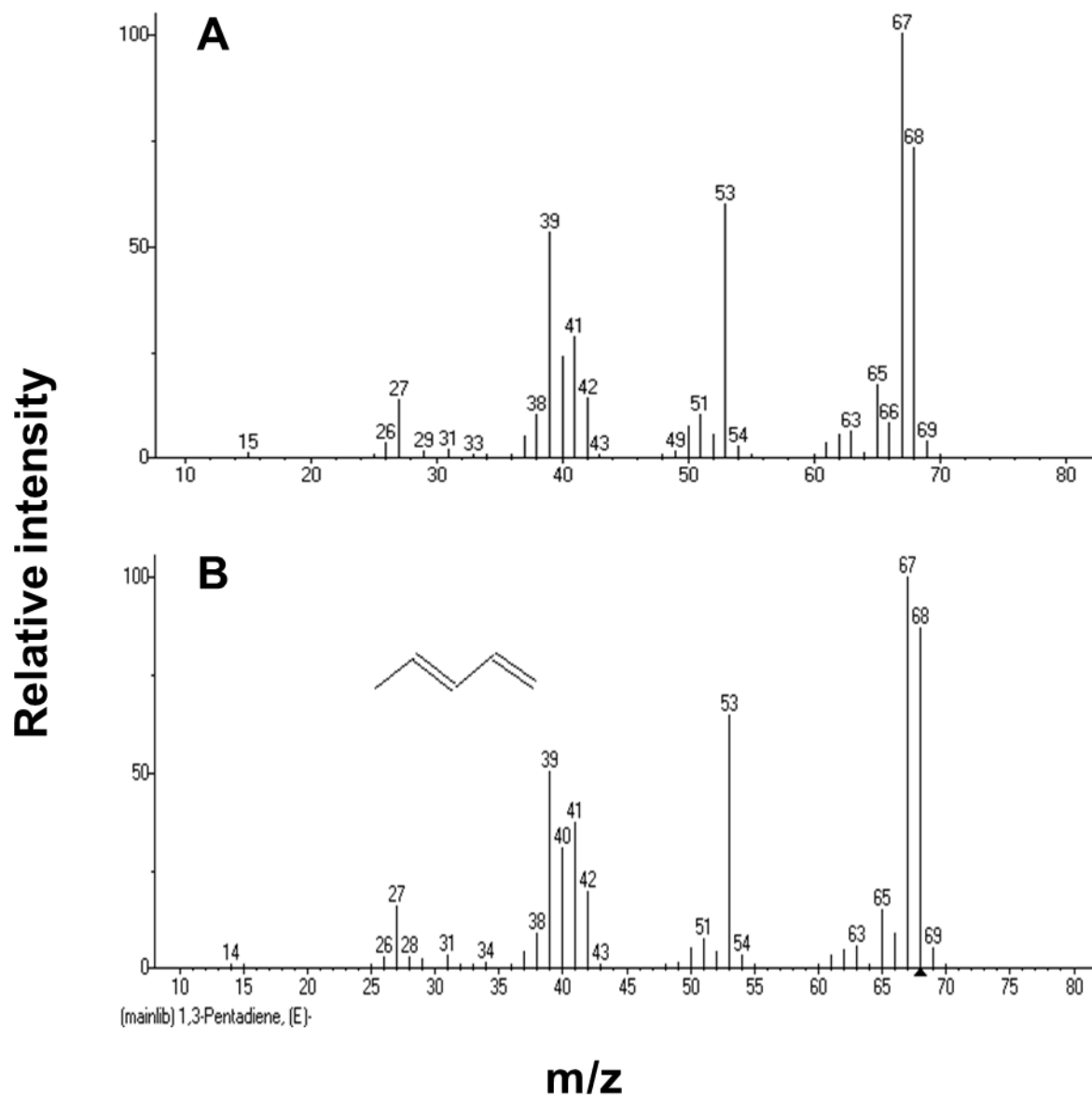


Figure S8. Mass spectrum fragmentation pattern of 1,3-Pentadiene **A** produced over P-SPP from 2-MTHF using the microcatalytic method at 400 °C **B** NIST mass spectrum fragmentation pattern library.

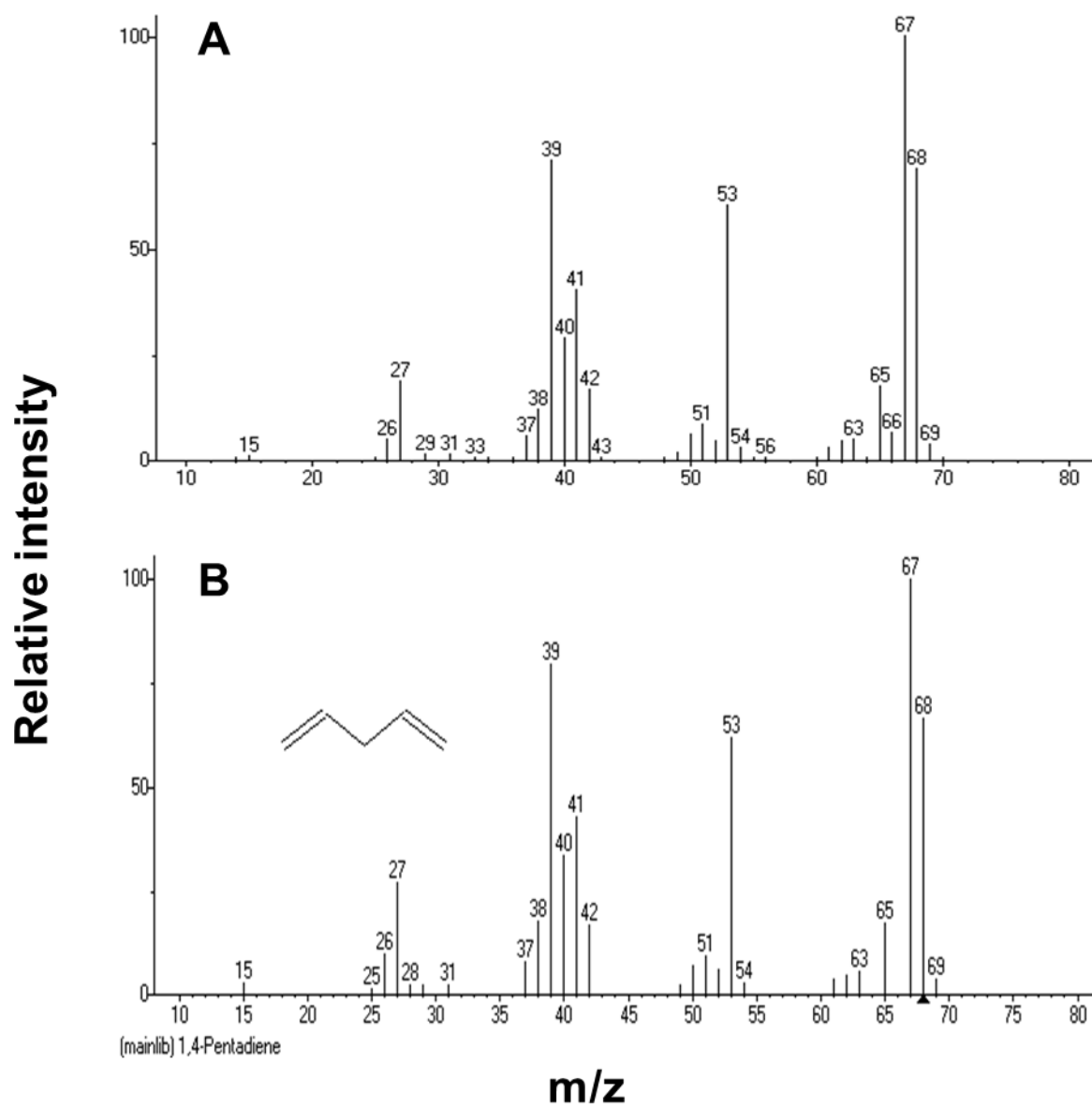


Figure S9. Mass spectrum fragmentation pattern of 1,4-Pentadiene **A** produced over P-SPP from 2-MTHF using the microcatalytic method at 400 °C **B** NIST mass spectrum fragmentation pattern library.

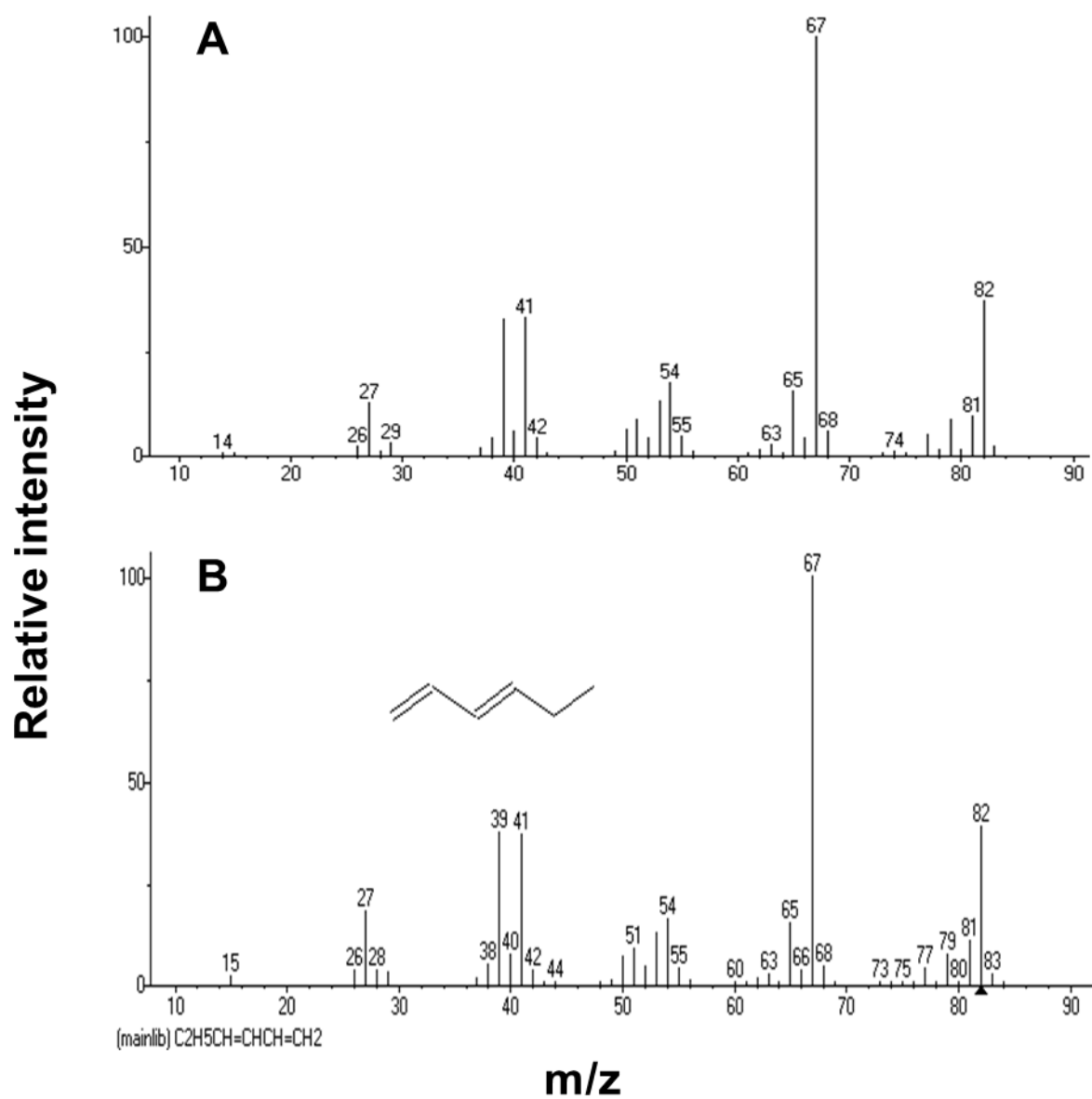


Figure S10. Mass spectrum fragmentation pattern of 1,3-Hexadiene **A** produced over P-SPP from 2,5-DMTHF using the microcatalytic method at 400 °C **B** NIST mass spectrum fragmentation pattern library.

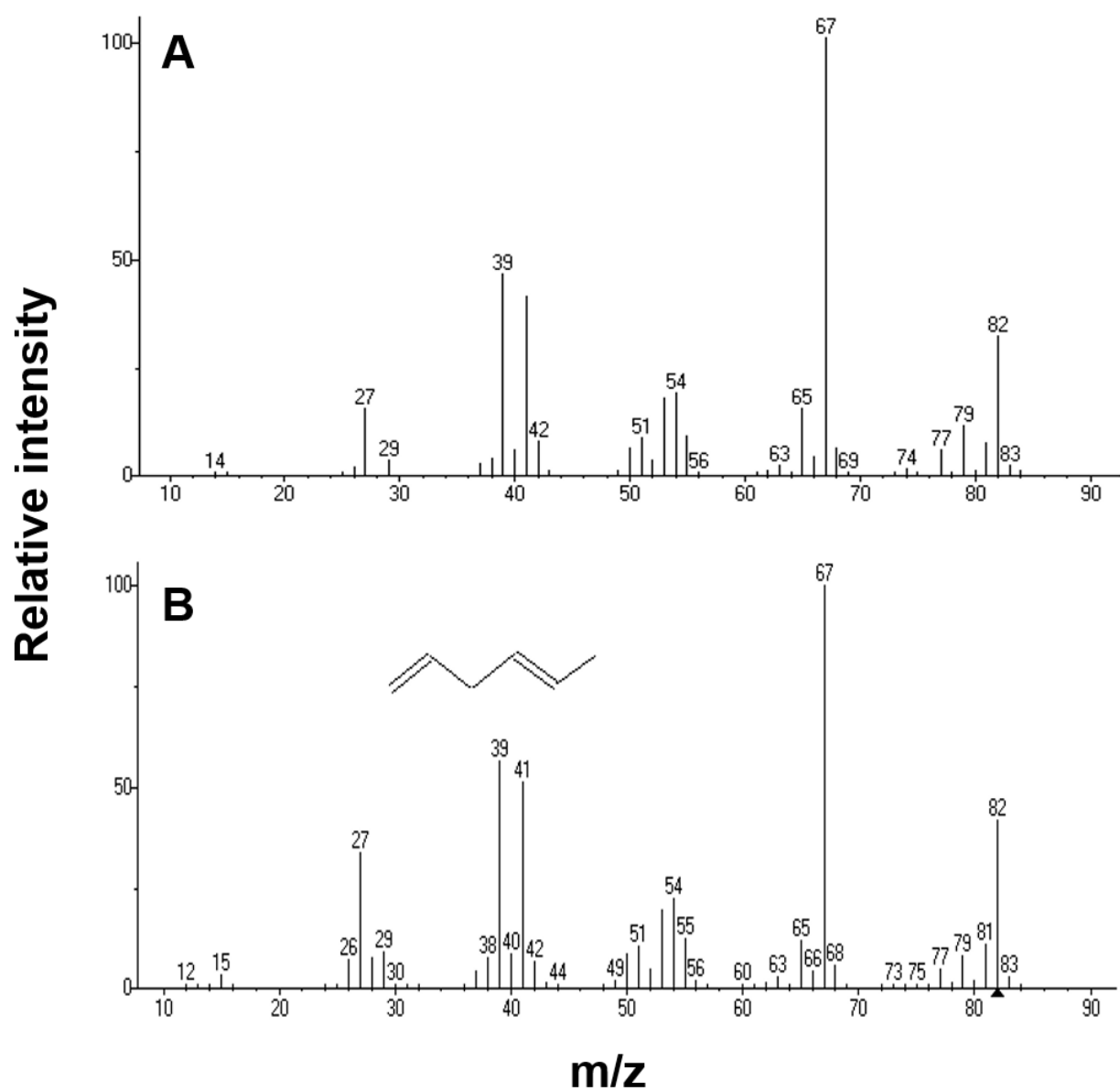


Figure S11. Mass spectrum fragmentation pattern of 1,4-Hexadiene **A** produced over P-SPP from 2,5-DMTHF using the microcatalytic method at 400 °C **B** NIST mass spectrum fragmentation pattern library.

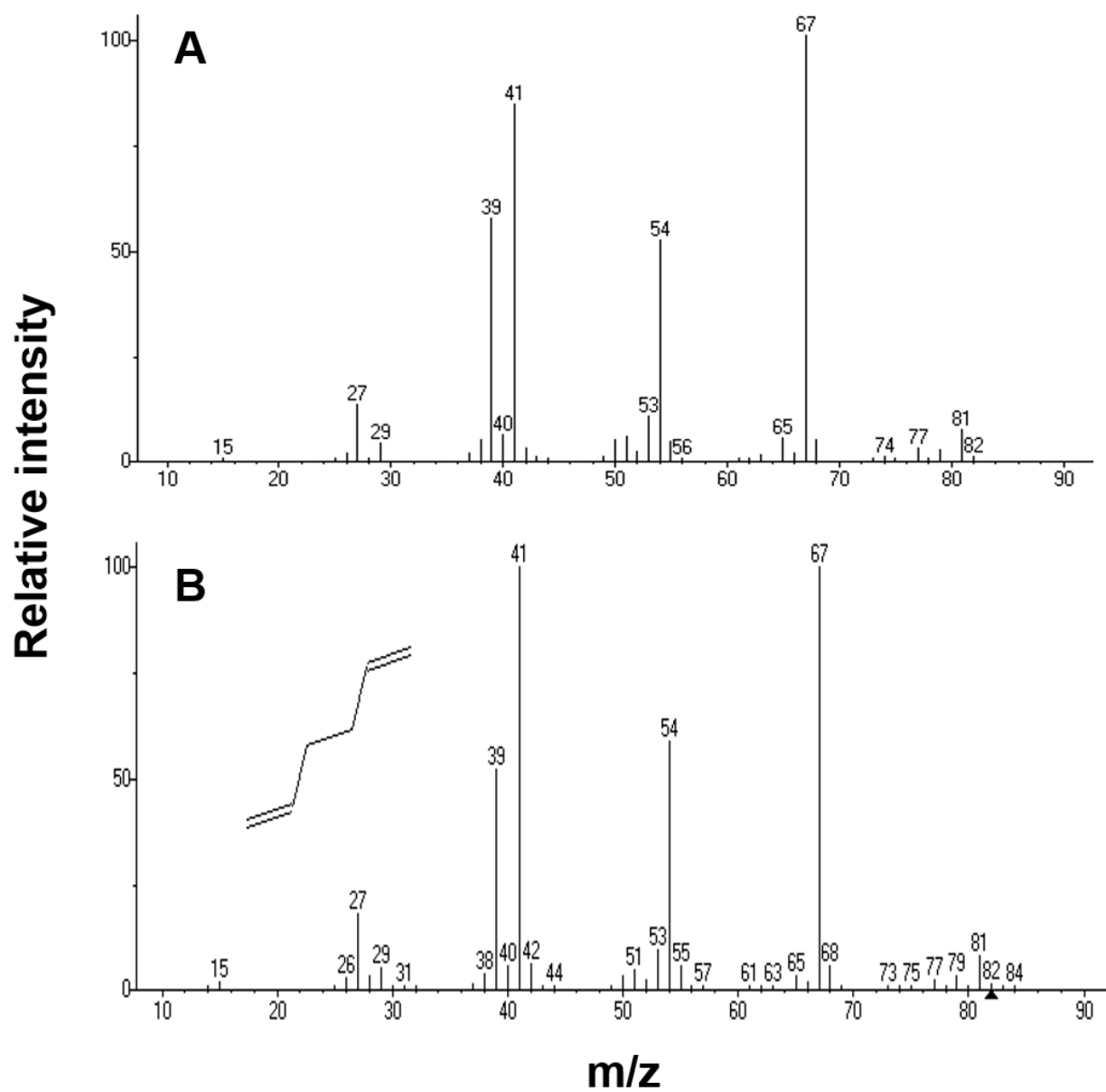


Figure S12. Mass spectrum fragmentation pattern of 1,5-Hexadiene **A** produced over P-SPP from 2,5-DMTHF using the microcatalytic method at 400 °C **B** NIST mass spectrum fragmentation pattern library.

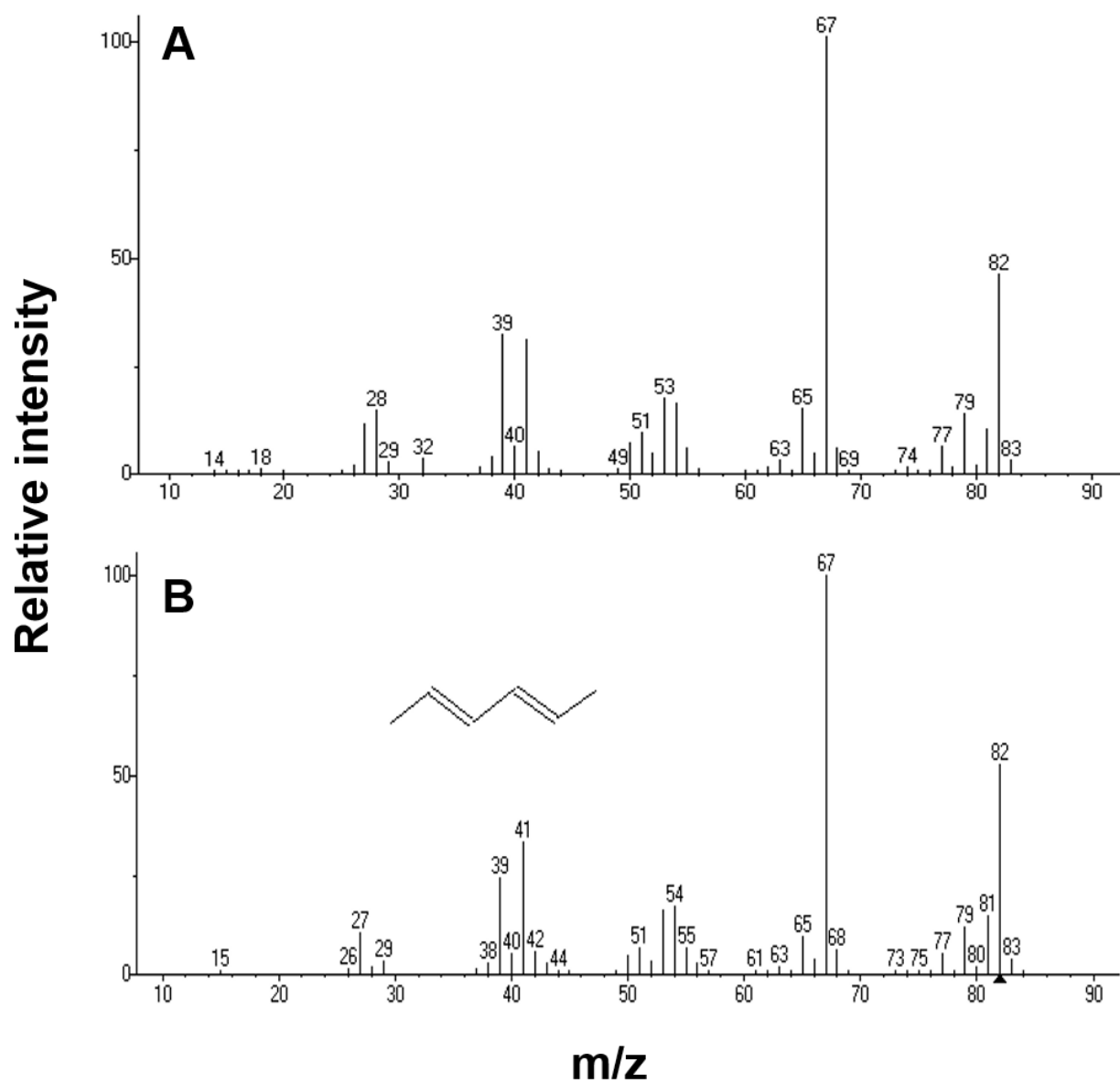


Figure S13. Mass spectrum fragmentation pattern of 2,4-Hexadiene **A** produced over P-SPP from 2,5-DMTHF using the microcatalytic method at 400 °C **B** NIST mass spectrum fragmentation pattern library.

12.0 Time-on-stream study of P-SPP catalyst

We evaluated the stability of P-SPP catalyst during the course of THF dehydrocyclization at 325 °C and a partial pressure of 5.5 torr. Shown in Figure S14 is the THF conversion profile with time-on-stream (TOS). The conversion of THF reduces from 49% initially to 18% after approximately 18 hours on stream. Despite the onset of deactivation leading to a loss in catalyst activity, the selectivity to butadiene remained constant at 94-95%. Throughout the 18 hr study, the carbon balance maintained an average value of 101.5 %.

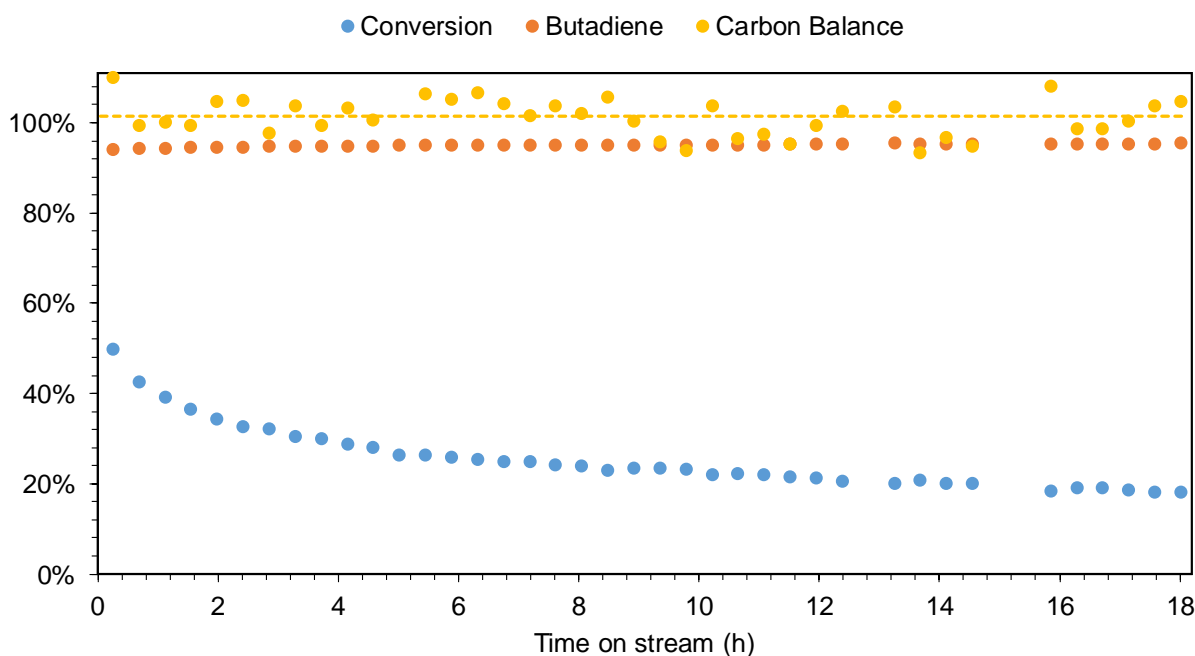


Figure S14. Time-on-stream study of isoprene production. The vapor-phase conversion (blue, ●) of tetrahydrofuran was selective to butadiene (orange, ●). The carbon balance (yellow, ●) of each experiment equals 100% within experimental error. Catalyst: P-SPP, Temperature: 325 °C, Partial pressure: 5.5 torr and WHSV = 0.1 g THF g cat⁻¹ hr⁻¹.

13.0 Apparent Reaction Barrier.

The reaction barriers of THF conversion to two products, butadiene and propene/formaldehyde, was measured with two catalysts, silica-alumina and P-SPP. Experiments were conducted at conversion of $X_{\text{THF}} < 25\%$ at temperatures of 250 to 350 °C. The feed partial pressure of THF was 5.0 torr in helium.

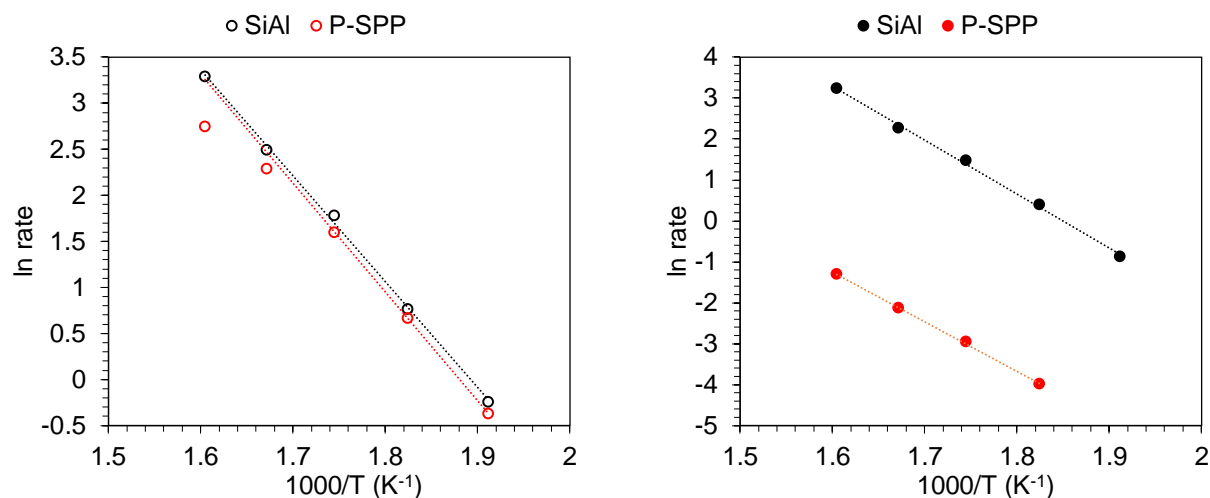


Figure S15. Apparent Reaction Barriers of THF Conversion on SiAl and P-SPP Catalyst. Left. The reaction of THF to produce butadiene and water occurs on Silica-Alumina and P-SPP at comparable mass-normalized rates (micromoles gram⁻¹ min⁻¹) with apparent barrier of $E_{a,\text{P-SPP}} 23.5 \pm 1.4$ kcal/mol and $E_{a,\text{SiAl}} 22.8 \pm 1.5$ kcal/mol. **Right.** The reaction of THF to produce propene and formaldehyde occurs on Silica-Alumina and P-SPP at different mass-normalized rates (micromoles gram⁻¹ min⁻¹) with apparent barrier of $E_{a,\text{P-SPP}} 24.1 \pm 1.9$ kcal/mol and $E_{a,\text{SiAl}} 26.2 \pm 2.2$ kcal/mol.

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