

Letter



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Biomass-Derived Butadiene by Dehydra-Decyclization of Tetrahydrofuran

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Abstract. Catalytic ring-opening dehydration of tetrahydrofuran (THF), itself a product of decarbonylation and reduction of biomass-derived furfural, yields 1,3-butadiene, an important monomer in rubbers and elastomers. It is demonstrated that dehydra-decyclization of THF with phosphorous-containing siliceous self-pillared pentasil (SPP) or MFI structure exhibits high selectivity to butadiene (85-99%) at both low (9%) and high (89%) conversion of THF. High selectivity to pentadiene and hexadiene was also obtained from 2-methyl-tetrahydrofuran and 2,5-dimethyl-tetrahydrofuran, respectively, with phosphorous-containing, all-silica zeolites.

Keywords: Butadiene, Tetrahydrofuran, Zeolite, Phosphorous, Pentadiene, Hexadiene, Dehydration

**Body Text.** Butadiene is a key monomer in many rubbery materials including co-polymers with unique product characteristics<sup>1</sup>. Polymerization of butadiene predominately in the *cis* conformation yields cis-1,4-polybutadiene which is a primary constituent of automobile tires. Butadiene can also be co-polymerized with styrene to produce styrene-butadiene rubber (SBR), which enhances abrasion resistance within tires. Additionally, butadiene co-polymerization with acrylonitrile forms NBR (nitrile butadiene rubber), a resilient rubber used for seals, hoses, and gloves. Co-polymerization with a third constituent forms ABS (acrylonitrile-butadiene-styrene), a hard thermoplastic molded into rigid shapes including Lego<sup>TM</sup> bricks<sup>2</sup>. Around 12 million tons of butadiene are produced worldwide for these polymer products from either n-butane dehydrogenation<sup>3</sup> or naptha cracking alongside numerous co-products including ethylene and propylene<sup>4,5</sup>.

On-purpose butadiene production from renewable sources remains a major target for sustainable chemical engineering. Competing pathways to butadiene from biomass have been extensively reviewed<sup>6</sup> with processes proposed through either ethanol or four-carbon alcohols. In the process first proposed by Ipatieff<sup>7</sup>, ethanol dehydrogenates to acetaldehyde followed by condensation to a four-carbon intermediate oxygenate (such as crotonaldehyde)<sup>8,9</sup>; subsequent deoxygenation results in butadiene selectivity as high as 70%<sup>6,10</sup>. Recent effort has predominately focused on the production of four-carbon diols (e.g., by fermentation of glucose<sup>11,12</sup>) followed by dehydration to butadiene. Dehydration of three isomers including 1,3-butanediol<sup>6,13</sup>, 2,3-butanediol<sup>6,14,15,16</sup>, and 1,4-butanediol<sup>6</sup> (1,4-BDO) have all demonstrated production of butadiene with a variety of metal oxide and solid acid catalysts<sup>6,17</sup>.

An alternative thermochemical pathway to butadiene depicted in Scheme 1 initially converts fivecarbon sugars such as xylose to furfural<sup>18,19</sup>, followed by decarbonylation and hydrogenation to tetrahydrofuran (THF)<sup>20,21</sup>. THF is a volatile (b.p. 66 °C) four-carbon cyclic ether which can then undergo ring-opening dehydration to butadiene and water. While the process in Scheme 1 obtains THF from furan, cyclo-dehydration of 1,4-BDO also produces THF selectively with numerous solid acid catalysts<sup>22</sup>; thus, dehydration of 1,4-BDO produces either 3-butene-1-ol or THF before further dehydration to butadiene. Vapor-phase dehydra-decyclization of THF has been demonstrated using a sodium phosphate catalyst which resulted in 31% butadiene yield at 375 °C<sup>23</sup>; however, the catalyst requires significant amounts of phosphorous<sup>24</sup>. Similarly, a V-Ti-P mixed oxide catalyst has been effective to catalytically dehydrate 2-methyl-tetrahydrofuran (2-MTHF) to pentadienes with yield as high as 63%<sup>25</sup>.

In this work, we evaluated phosphorous-containing siliceous zeolites for the selective dehydration and ring opening of tetrahydrofuran (THF) to butadiene; these catalysts were recently demonstrated for the selective dehydration to p-xylene<sup>26</sup> from dimethylfuran and ethylene. As depicted in Figure 1, dehydradecyclization of THF to produce butadiene occurs in competition with two side reactions. Ring opening of THF without dehydration produces 3-butene-1-ol by an overall thermodynamically unfavorable reaction ( $\Delta G$  of +5 to +7 kcal mol<sup>-1</sup>) for relevant reaction temperatures (25-400 °C). Alternatively, reaction of THF produces propylene and formaldehyde, presumably by the reverse Prins condensation reaction<sup>27</sup> ( $\Delta G$  of -6 to +9 kcal mol<sup>-1</sup>). Despite these competing pathways, reaction to butadiene is most favorable ( $\Delta G$  of -14 to +1 kcal mol<sup>-1</sup>) at relevant conditions (25-400 °C).

Experiments were conducted in two experimental reactor systems: a pulsed microcatalytic reactor for screening of catalysts and a packed bed continuous flow reactor for evaluation of catalyst performance. In the first method, evaluation of a wide range of conditions and catalysts was conducted using the previously described 'microcatalytic method'<sup>28,29</sup>; a pulse of reactant flowed over a fixed bed of catalyst particles to determine the conversion, yield of products, or kinetics of catalytic chemistry<sup>30,31</sup>. The data of Figure 2 were obtained by utilizing the microcatalytic method via the automated operation of a gas chromatograph (GC). Solid acid catalyst particles were prepared as a packed bed held between quartz wool plugs within a GC inlet liner (Fig. S2). Evaluation of the GC inlet microcatalytic reactor demonstrated repeatable control (200-400 °C) and reactant gas/vapor flow rates (organic compounds and helium carrier gas) of 6.0-1200 sccm (space velocities of 0.2-130 s<sup>-1</sup>). Experiments consisted of a 1.0  $\mu$ L liquid injection of THF, 2-MTHF or 2,5-dimethyl-tetrahydrofuran (2,5-DMTHF) with a GC autosampler. The injected liquid sprayed over the quartz packing, evaporated, and flowed over the catalyst bed; the resulting products then exited the GC inlet liner and entered the GC column/detector for separation and quantification. Complete details are available in the supporting information.

Evaluation of the dehydra-decyclization of THF indicated significant variation of catalyst activity and selectivity to butadiene for the considered temperature range, 200-400 °C, and space velocity, 0.2-90 s<sup>-1</sup>, as shown in Figure 2. Catalysts such as Sn-BEA, zirconium oxide (ZrO<sub>2</sub>), niobium oxide (Nb<sub>2</sub>O<sub>5</sub>), and phosphotungstic acid (PWA) were all relatively inactive compared with silica alumina (SiAl), aluminum-containing faujasite, ZSM-5, and phosphorous-containing self pillared pentasil (P-SPP). H-Y and ZSM-5 exhibited only low selectivity to butadiene (<30%) at conversions above 10%. Silica alumina was more selective (71%) at 19% conversion of THF, but selectivity to butadiene reduced significantly at higher conversion (>40%). In contrast, P-SPP was highly selective (85-99%) at both low (9%) and high (89%) conversion of THF. Complete experimental results are available in the supporting information.

Ring-opening dehydration of THF was further evaluated with five different phosphorous-containing catalysts in Figure 3A. Sodium phosphate (Na<sub>3</sub>PO<sub>4</sub>) was not selective to butadiene and exhibited low overall activity consistent with previous reports that metal-phosphates required long residence times<sup>24</sup>. Phosphorous aluminum beta (P-Al-BEA) exhibited significant activity (e.g.  $X_{THF}$ >99%) but with only limited selectivity to butadiene (S<40% for  $X_{THF}$ >20%). In contrast, P-SPP, P-MFI, and P-BEA were all

highly selective to butadiene. Side products included propylene, formaldehyde, butenes and other unidentified species quantified by the quantitative carbon detector (QCD) method<sup>32</sup>.

Additional experiments (Scheme 1B and 1C) evaluated the ring-opening dehydration of substituted THF including 2-MTHF to 1,3- and 1,4-pentadienes and 2,5-DMTHF to hexadienes. Dehydradecyclization of 2-MTHF and 2,5-DMTHF reactants was evaluated with P-SPP catalyst using the microcatalytic method as depicted in Figure 3B. Selectivity to C5 and C6 dienes was high (>70%) for all extents of conversion up to 90%, but the produced dienes were a mixture of isomers. For example, as depicted in the inset bar graph of Fig. 3B, reaction of 2-MTHF produced primarily 1,3-pentadiene (*cis* and *trans*) with a small amount of 1,4-pentadiene. Eight different isomers of straight-chain hexadienes were also measured by gas chromatography (Figure S10-13).

The optimal catalysts (P-containing zeolites) and conditions identified by screening with the microcatalytic method in Figures 2 and 3 were further evaluated using a packed-bed continuous flow reactor as shown in Figure 4. The packed bed reactor was comprised of a stainless steel tube (1/2") within an aluminum cylinder heated with a furnace. The reactor system was validated by comparison with existing isopropanol dehydration kinetics prior to use to ensure reaction kinetic control (Figure S3). As depicted in Figure 4A, selectivity to butadiene from THF remained high (>95%, P-SPP) under steady-state operation, while Sn-BEA, silica alumina and ZSM-5 all exhibited lower selectivity to butadiene. The P-SPP catalyst performance was evaluated at lower weight hourly space velocity (WHSV) in Figure 4B to show that selectivity to butadiene remained high (87-92%) at higher conversion (53% <  $X_{THF}$  < 83%) of THF. Evaluation at higher THF reactant partial pressure (50 torr), at conditions more relevant to industrial processes<sup>25</sup>, did not alter the selectivity to butadiene. Additionally, evaluation of 2-MTHF in the continuous flow reactor resulted in similar high selectivity to pentadienes (Fig. 4C) with P-SPP catalyst. Complete experimental details are available in the supporting information.

An efficient process to renewable C4-C6 dienes can potentially enable a rubber/elastomer industry based on abundant biomass-derived feedstocks. The process chemistry described in Scheme 1 provides an entirely thermochemical pathway from lignocellulose to dienes with highly selective process steps. The last step to butadiene and larger dienes is enhanced by the newly introduced class of catalysts, phosphorous-containing all-silica zeolites, similar to the dehydra-decyclization of 3-methyl-tetrahydrofuran to isoprene with P-SPP<sup>33</sup>. However, additional studies of reaction kinetics and catalyst characterization are necessary to understand the active site structure of these materials, the role of phosphorous, and the detailed reaction mechanism.

#### ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: X

Materials and methods, thermodynamic calculations, screening of reaction conditions, detailed reaction results, product identification by gas chromatograph-mass spectrometry (GC-MS), and long-term stability testing.

## ACKNOWLEDGEMENTS

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Scheme 1. Dehydra-Decyclization of Tetrahydrofurans. A. Xylose dehydration to furfural, followed by decarbonylation and hydrogenation to tetrahydrofuran. Dehydration and ring-opening produces butadiene. B. Methyl-tetrahydrofuran dehydration and ring-opening to pentadienes. C. Dimethyl-tetrahydrofuran dehydration and ring-opening to hexadienes.





**Figure 1. Vapor-Phase Thermochemistry of Dehydra-Decylization of Tetrahydrofuran.** The three main reactions of tetrahydrofuran with solid acid catalysts produce propene and formaldehyde (red), butadiene and water (blue), and 3-butene-1-ol (black). Gibbs free energies of the three classes of products indicate favorable formation of butadiene at equilibrium (Supporting Information, Table S3).





**Figure 2. Dehydra-decyclization of tetrahydrofuran to butadiene.** Vapor-phase reactions evaluated by the microcatalytic method at 200-400 °C and space velocities of 1-90 s<sup>-1</sup> with solid acid catalysts: Phosphorous Self-Pillared Pentasil (P-SPP, **•**), Faujasite (H-Y, •), ZSM-5 (**•**), Silica-Alumina (SiAl, **•**), Niobium Oxide (Nb<sub>2</sub>O<sub>5</sub>, **•**), Sn-BEA ( $\circ$ ), Zirconium Oxide (ZrO<sub>2</sub>,  $\diamond$ ), Phosphotungstic Acid (PWA, •). Additional details in the supporting information.



**Figure 3. Dehydra-decyclization of THF, 2-MTHF, and 2,5-DMTHF. A.** Vapor-phase reactions evaluated by the microcatalytic method at 200-400 °C and space velocities of 0.2-130 s<sup>-1</sup> with solid acid catalysts: Phosphorous Self-Pillared Pentasil (P-SPP,  $\blacksquare$ ), P-MFI ( $\bullet$ ), P-BEA ( $\bullet$ ), P-Al-BEA ( $\blacktriangle$ ), Sodium Phosphate (Na<sub>3</sub>PO<sub>4</sub>,  $\circ$ ). **B.** Vapor-phase reactions with P-SPP catalyst at 200-400 °C and space velocities of 0.2-90 s<sup>-1</sup> substituted reactants including tetrahydrofuran (THF,  $\blacksquare$ ) to make butadiene, 2-methyl-tetrahydrofuran (2-MTHF,  $\blacktriangle$ ) to make pentadienes, and 2,5-dimethyl-tetrahydrofuran (2,5-DMTHF,  $\bullet$ ) to make hexadienes. **B-Inset:** Selectivity to 1,3-and 1,4-pentadienes from 2-MTHF with P-SPP catalyst at 10 s<sup>-1</sup>. Additional details in the supporting information.



**Figure 4. Dehydra-decyclization in a Catalytic Packed Bed Flow Reactor. A.** Reaction of tetrahydrofuran to butadiene at 250-350 °C, WHSV=1.0 hr<sup>-1</sup> and 4.9 torr with catalysts: P-SPP (**■**), Sn-BEA (**■**), Silica Alumina (SiAl, **■**), and ZSM-5 (**■**). **B.** Reaction of tetrahydrofuran to butadiene at 350-400 °C, 4.9 torr, with P-SPP catalyst at varying WHSV. **C.** Reaction of 2-methyl-tetrahydrofuran to 1,3- and 1,4-pentadienes at 250-300 °C, WHSV=1.0 hr<sup>-1</sup> and 4.9 torr with catalysts: P-SPP (**■**) and Silica Alumina (SiAl, **■**). Conversion for each experiment noted numerically within each bar; complete details in the supporting information.

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Dehydra-decyclization of biomass-derived tetrahydrofuran provides a chemical process to manufacture butadiene from renewable resources.



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Figure 3 203x85mm (300 x 300 DPI)

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