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Ring Opening of Biomass-derived Cyclic Ethers to Dienes over Silica/Alumina

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ABSTRACT

We show that cyclic ethers, such 2-methyltetrahydrofuran (2-MTHF), can undergo dehydration to produce pentadienes over SiO_2/Al_2O_3 . The catalyst exhibited reversible deactivation due to coke deposition, with the yield to pentadienes decreasing from 68% to 52% at 623 K over 58 h time on stream. A reaction network for 2-MTHF dehydration was proposed based on the results of space time studies. Pentadienes can be produced directly by concerted hydride-shift and dehydration of carbenium intermediates or indirectly through dehydration of pentanal and penten-ol. Reaction kinetics studies were performed at temperatures ranging from 573 to 653 K and 2-MTHF partial pressures from 0.21 to 2.51 kPa. The apparent activation energy barrier for 2-

MTHF conversion to pentadienes and the reaction rate order for ring opening were determined to be 74 kJ mol⁻¹ and 0.24, respectively, indicating strong interaction between 2-MTHF and the SiO₂/Al₂O₃ surface. Other solid acids such as γ -Al₂O₃, H-ZSM-5, Al-Sn-Beta were found to be active for 2-MTHF dehydration to pentadienes. The rate of ring opening decreased in the order: 2,5-dimethyltetrahydrofuran > 2-MTHF > tetrahydropyran > tetrahydrofuran. Over SiO₂/Al₂O₃, the dehydration of 2,5-dimethyltetrahydrofuran resulted in 75% yield to hexadiene isomers.

GRAPHICAL ABSTRACT



KEYWORDS

2-methyltetrahydrofuran, dehydration, pentadiene, reaction network, solid acids, reversible deactivation

INTRODUCTION

Lignocellulosic biomass has recently received considerable interest as a renewable feedstock for the production of platform molecules which can subsequently be converted to fuels and value-added chemicals.^{1,2} One such molecule, 2-methyltetrahydrofuran (2-MTHF) has gained attention as a green solvent or as a gasoline additive.^{3,4} 2-MTHF can be obtained from biomass-derived intermediates such as levulinic acid and furfural.⁵ The pentoses in lignocellulose can be converted to furfural using acid hydrolysis.⁶⁻⁸ Furfural can undergo hydrodeoxygenation to 2-MTHF in high yield in a single step over silica-supported Pd and Cu catalysts.⁹ 2-MTHF is also a monofunctional intermediate produced during aqueous phase hydrodeoxygenation of sorbitol over catalysts such as Pt-Re/C and Pd-Ag/WO_x-ZrO₂.^{10,11} In our on-going work of aqueous phase hydrodeoxygenation of sorbitol over Co/TiO₂, these monofunctional intermediates consist mainly of alcohols (69% of the carbon in monofunctionals) and heterocyclic species (23% of the carbon in monofunctionals). These monofunctional compounds can then undergo C-C bond formation followed by hydrodeoxygenation to produce jet and diesel range blendstocks.^{2,12} The monofunctionals can also be fed to an acidic catalyst to produce olefins, which can then be converted into jet and diesel fuel by oligomerization and hydrogenation reactions. In our current work, we remove the oxygen from these monofunctional compounds via dehydration using a solid acid catalyst. In addition to the monoalkenes formed by dehydration of the alcohol fraction, dienes were also observed in the effluent stream. We then performed studies over this solid acid using 2-MTHF as the model heterocyclic and observed the formation of 1,4-pentadiene and 1,3-pentadiene isomers. There is limited work reported on the dehydration of cyclic ethers to dienes. The objective of this work, therefore, is to understand the

reaction network as well as the factors that affect the activity of the solid acid for this acidcatalyzed reaction.

1,3-Pentadiene, commercially known as piperylene, is a reactive linear hydrocarbon. Piperylenes are by-products of the petroleum industry and are widely used as monomers in the production of adhesives, plastics, and resins. The conjugated dienes serve as substrates for conversion into highly functionalized molecules via organic reactions, e.g. Diels-Alder, hydroformylation, and carbonylation.^{13,14} Currently, the main source of C₅ hydrocarbons is steam cracking of naphtha obtained from crude oil. The separation of C₅ hydrocarbons is achieved using extractive rectification and metal-organic frameworks.¹⁵ Besides the crude oil route, majority of literature for piperylene production involves processes using thermochemical methods and homogeneous catalysis. Geller and Schniepp observed that pyrolytic decomposition of 1,5-pentanediol diacetate yielded 1,4-pentadiene with 90-96% purity at 848 K.¹⁶ Brookhart and co-workers have reported ~40% yield to piperylenes via transfer dehydrogenation of pentane using iridium pincer complex.¹⁷ Recently, Goldman and co-workers have reported high yields $(\sim 70\%)$ to pipervlenes for the same reaction catalyzed by pincer-ligated iridium complexes.¹⁸ These homogeneous catalysts, however, have separations costs associated with them and have challenges for large scale applications.

An alternative and renewable route to produce pentadienes would be to employ heterogeneous catalysts for conversion of biomass-derived platform chemicals. Chia and Dumesic have studied a process for conversion of 4-hydroxy-6-methyl-2-pyrone to 6-methyl-5,6-dihydro-2-pyrone and used acid-catalyzed ring opening of the latter compound to produce 2,4-hexadienoic acid and 1,3-pentadiene.¹⁹ The advantage of this method is that the starting material can be made from a renewable precursor, such as biomass-derived glucose using

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recombinant bacteria or yeast. Another process would be the conversion of C₅ cyclic ether, 2-MTHF, obtained in good yield from lignocellulose-derived pentoses. Oyama and co-workers have reported ~33% yield of pentadienes during the hydrodeoxygenation of 2-MTHF over WP/SiO₂ at 623 K.²⁰ Johns developed a process consisting of two-step hydrogenation of furfural to 2-MTHF using Cu and Ni catalysts and subsequently dehydrating 2-MTHF over a phosphate salt at temperatures near 600 K to obtain 1,3-pentadienes with small amount of 1,4-pentadiene.²¹ Norman has reported the dehydration of 2-MTHF to piperylene in high yield over vanadiumtitanium-phosphorous ternary mixed oxide and boron phosphate.²² Over V-Ti-P oxide, 80% of 2-MTHF is converted to 1,4-pentadiene and 1,3-pentadiene with 81.4% total selectivity i.e. 65.1 % yield at 623 K and atmospheric pressure. The side products reported are 4-penten-2-ol, 3-penten-2-ol, and an unknown fraction. Diene polymerization leads to formation of coke and subsequent catalyst deactivation. Dehydration of tetrahydropyran and 3-methyltetrahydrofuran to pentadiene and isoprene was carried out, but the activity was lower as compared to that for 2-MTHF. Recently, the dehydra-decyclization of tetrahydrofuran and 3-methyltetrahydrofuran to butadiene and isoprene, respectively, over phosphorous self-pillared pentasil has been reported by Abdelrahman et al.^{23,24}

In this work, the vapor-phase dehydration of 2-MTHF to pentadienes was investigated over various solid acids, particularly over amorphous SiO_2/Al_2O_3 . Silica/alumina has been demonstrated to be active and stable during dehydration of 1-butanol and decarboxylation of γ -valerolactone in high water environments.^{10,25} Dauenhauer and co-workers have observed higher yield to pentadienes during 2-MTHF dehydration over SiO_2/Al_2O_3 as compared to phosphorus-containing siliceous self-pillared pentasil.²³ Space velocity studies were performed to probe the reaction network for the ring opening of 2-MTHF. The effects of temperature and partial

pressure of the reactant on the activity of 2-MTHF are also discussed. In addition to 2-MTHF, ring opening of other cyclic ethers, namely, tetrahydropyran, tetrahydrofuran, and 2,5-dimethyltetrahydrofuran to their respective dienes was investigated. This conversion of cyclic ethers can serve as a potential route to make dienes from biomass.

EXPERIMENTAL DETAILS

Materials and Characterization

The cyclic ethers, 2-methyltetrahydrofuran (2-MTHF, Sigma-Aldrich, >99%, 250 ppm butylated hydroxytoluene as stabilizer), 2,5-dimethlytetrahydrofuran (2,5-DMTHF, Sigma-Aldrich, 96%), tetrahydrofuran (THF, Sigma-Aldrich, >99.9%, BHT as stabilizer), and tetrahydropyran (THP, Sigma-Aldrich, 99%) were used as purchased without further purification.

Amorphous SiO₂/Al₂O₃ (13.7 wt% alumina content) obtained from Grace Davision (Grade 135) was used for the ring opening of various heterocyclics to dienes. The catalyst was calcined *ex situ* at 773 K (2 K min⁻¹, 2 h) in flowing air (Airgas, 50 cm³ min⁻¹). The BET surface area was obtained from the nitrogen adsorption isotherms carried out in a volumetric adsorption unit (Micromeritics, ASAP 2010). The catalyst was degassed at 423 K in vacuum for 6 h prior to the measurements. The surface area and mean pore diameter for the catalyst were calculated to be 450 m² g⁻¹ and 5.4 nm, respectively. Ring opening of 2-MTHF was also investigated over various solid acids like H-ZSM-5 (SiO₂:Al₂O₃ = 23), H-Mordenite (H-MOR, SiO₂:Al₂O₃ = 20), H-Beta (H-BEA, SiO₂:Al₂O₃ = 25) (Zeolyst International), γ -Al₂O₃ (Strem Chemicals), Al-Sn-

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Beta (Al-Sn-BEA, Si/Sn=200, Si/Al= 50, Haldor Topsøe A/S, Denmark), NbOPO₄, and Nb₂O₅ (CBMM, Brazil).

The total and Brønsted acid site densities on the catalyst were estimated using ammonia temperature-programmed desorption (NH₃-TPD) and isopropylamine temperature-programmed desorption (IPA-TPD), respectively (Micromeritics, Autochem II 2920). Approximately 100 mg of sample was loaded in a quartz cell and pretreated in He at 773 K. For NH₃ adsorption, the sample was cooled to 423 K after pretreatment, saturated with NH₃ for 1 h and then flushed with He for 1 h to remove the physisorbed ammonia. The TPD was performed using a temperature ramp of 10 K min⁻¹ from 423 K to 973 K under flowing He. The amount of ammonia desorbed was calculated by integrating the thermal conductivity detector signal. For IPA-TPD, the IPA was dozed in pulses over the sample at 323 K until saturation after which the cell was purged with He for 1 h. During TPD, the propene evolved via IPA decomposition was quantified to determine the Brønsted acid site density.

Reactivity Measurements

The ring opening of various heterocyclics was studied in gas-phase in a fixed-bed downflow reactor (Supporting Information, Figure S1) at atmospheric pressure and temperatures varying from 573 to 653 K. The catalyst was packed in a stainless steel tubular reactor (6.35 mm OD) between plugs of quartz wool and quartz beads. A well-insulated furnace (Applied Test Systems) was used as the heat source and aluminium blocks were used around the reactor to ensure isothermal operation. Reactor temperature was monitored at the reactor wall using a Ktype thermocouple (Omega) and 16A series programmable PID controller (Love Controls). For the first set of reactions using dodecane as the solvent, 1-20 wt% of 2-MTHF in dodecane was introduced in the reactor using an HPLC pump (Lab Alliance Series I). Helium (Airgas) was

used as the carrier gas, and the flow rates were adjusted using a mass flow controller (Brooks Instruments). The reactor effluent was passed through a gas-liquid separator immersed in an icewater bath to ensure that condensation of low-boiling products does not take place in the tubing connected to the gas GC. Gas-phase products were purged from the separator by flowing He and were analysed using an online GC-FID (Agilent) and a GC-2014 (Shimadzu) equipped with a TCD using He as the reference gas. Periodic liquid drains were collected from the separator and injected in a GC-2014 (Shimadzu). Total carbon balances are typically closed to within 10%. Both the gas and liquid products were identified using a GC-MS (Shimadzu, QP-2010).

A control experiment was carried out to ensure that the solvent was inert. Using pure dodecane as the feed and the same reaction conditions over SiO₂/Al₂O₃, we did not observe any dodecane conversion. Similarly, to verify that the conversion of 2-MTHF to pentadiene is indeed catalytic, a reaction was performed at 623 K using a control bed in the absence of a catalyst and no 2-MTHF conversion was observed. The reaction kinetics studies were performed in the absence of external and internal mass transfer limitations and the criteria for the same are reported in the Supporting Information.

The reaction network was probed using space velocity measurements where the product selectivities versus reciprocal space velocity (equal to space time) reveal the sequence of product formation. The space times were varied by altering the catalyst amount and the reactant flow rate. Weight hourly space velocity (WHSV) was defined as the mass of the feed molecule per mass of catalyst per hour and the space time was defined as inverse of WHSV (Equation (1)). The helium flow rate was chosen such that the molar ratio of 2-MTHF:He was kept constant. The rate of production of various products was plotted against the space time to determine the

primary and secondary products. The space time experiments were carried out in the kinetic regime over SiO_2/Al_2O_3 at a constant temperature of 623 K.

Space time (h) =
$$\frac{1}{\text{WHSV}(h^{-1})} = \frac{\text{Mass of catalyst (g)}}{2\text{-MTHF flow rate (g h^{-1})}}$$
 (1)

Gaussian09 software²⁶ was used for thermodynamic calculations. Geometry optimizations and subsequent frequency calculations were performed using B3LYP/6-311+G(2d,p). Frequency calculations provided estimates for standard changes of enthalpy, entropy, and Gibbs free energy, which were used in estimating thermodynamic properties over the range of temperatures used in this study.

The apparent activation energy for pentadiene formation was calculated over the temperature range from 573 to 653 K. The reaction rate order with respect to 2-MTHF was obtained by varying its partial pressure. All solid acid catalysts were observed to undergo deactivation as the reaction progressed. Each data set was collected within 10 h of the start of the experiment and the initial rates were obtained by extrapolation to time zero. For SiO₂/Al₂O₃, we observed that initial activity could be restored completely upon calcination in air at 773 K.

For the second set of reactions without using any solvent, low flow rates of the cyclic ethers were achieved using a syringe pump (Harvard Apparatus, PHD Ultra) and helium was used as a carrier gas. The products were analysed by an online GC equipped with a barrier discharge ionization detector (GC-BID, Shimadzu). All the lines from the reactor to the gas GC were heat traced and were maintained at 423 K to prevent condensation of the products and reactants.

RESULTS AND DISCUSSION

2-MTHF Conversion over SiO₂/Al₂O₃

The dehydration of 2-MTHF over SiO₂/Al₂O₃ was investigated at 623 K and atmospheric pressure. We observed the formation of *cis* and *trans*-1,3-pentadiene, 1,4-pentadiene, pent-enols, pentanal, pent-en-als, butenes as well as C₂-C₃ alkenes. The conversion of 2-MTHF to *trans*-1,3-pentadiene is an endothermic reaction with Δ H^o of 45.8 kJ mol⁻¹ and is highly favourable at 623 K (Δ G^o = -76.8 kJ mol⁻¹). A reaction at high conversion of 2-MTHF was performed to determine the yield to pentadienes. The catalyst undergoes continuous deactivation and the 2-MTHF conversion decreases from 100% to 77% over a period of 58 h (Figure 1). The yield towards pentadiene decreases from 67.8% to 51.8%. The initial yield to pentadienes is comparable to that observed by Norman over V-Ti-P oxide.²² The 1,3-pentadiene (*cis* and *trans* combined) and 1,4-pentadiene yields at 58 h are 41.5% and 10.3%, respectively. Brønsted acid catalysts are known to catalyze double bond isomerization and the higher yield towards the conjugated diene, 1,3-pentadiene can be explained owing to its higher stability as compared to 1,4-pentadiene.²⁷



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Figure 1. 2-MTHF conversion and yield to pentadienes over SiO_2/Al_2O_3 . Reaction conditions: 1.0 g catalyst, 10 wt% 2-MTHF in dodecane, 30 cm³ min⁻¹ He, 623 K, 1 atm, WHSV: 0.18 h⁻¹.

Reaction Pathways

The reaction network for ring opening of 2-MTHF to pentadiene was probed using space time studies. Figure 2 shows the effect of space time on the selectivity of various products identified in the reaction. The pentadienes (Figure 2(a)) show non-zero initial product selectivity, indicating that they are primary products and are formed directly from 2-MTHF. The selectivity for production of pentadienes also increases with time on stream, suggesting that they can also be formed as secondary products. The selectivity to pent-en-ol and pentanal (Figure 2(b)) at low space times are also non-zero, exhibiting primary product behaviour. The selectivity to pent-enol decreases from 19.1% to 7.9% as the space time increases from 10.7 s to 101.3 s, showing that pent-en-ol undergoes further conversion. The selectivity for 1-butene increases with space time, showing an apparent secondary product behaviour. In addition to these products, the formation of pentenes, pent-en-als and C_2 - C_3 alkenes was observed.



Figure 2. Product selectivities vs space times for 2-MTHF ring opening over SiO_2/Al_2O_3 . Reaction conditions: 20 wt% 2-MTHF in dodecane, 623 K, 1 atm, WHSV: 35.5- 336 h⁻¹. (a) Carbon selectivity to primary product, pentadiene, versus reciprocal space velocity; (b) Carbon selectivities to minor products pent-en-ol, butene, and pentanal versus reciprocal space velocity.

There are two positions where the C-O bond can undergo cleavage on 2-MTHF, forming either 2-pentanone or pentanal. The GC-MS fragmentation patterns obtained for carbonyl compounds in the liquid drain confirmed the presence of pentanal. Primary and secondary carbenium ions can be formed during formation of 2-pentanone and pentanal, respectively. Since a secondary carbenium is more stable than a primary carbenium, pentanal formation is favored over that of 2-pentanone. To probe the rate of formation of dienes from pentanal, we conducted experiments with pentanal in dodecane feed, maintaining the same partial pressure as that for 2-MTHF during the space time studies. The specific rate of pentadiene formation from pentanal was 26 µmol g⁻¹ min⁻¹ which is 30 times lower compared to the pentadiene formation from 2-MTHF (740 µmol g⁻¹ min⁻¹) under similar reactions conditions. Also, pent-en-ol formation was not observed during pentanal conversion.

As seen in Figure 2, butene selectivity increases with space time as that of pent-en-ol decreases. We propose that a fraction of pent-en-ols is converted to butene and formaldehyde via reverse Prins reaction over the Lewis acid sites in SiO₂/Al₂O₃. The amount of formaldehyde could not be quantified using GC-FID, but the presence of formaldehyde was confirmed using GC-MS. For quantification, moles of formaldehyde were assumed to be equal to the moles of butene. The Prins reaction involves condensation of an aldehyde with an alkene, resulting in the formation of unsaturated alcohols, alkyl dioxanes, and dienes. This acid-catalyzed reaction is traditionally catalyzed by homogeneous mineral acids, Lewis acids like SnCl₄, as well as solid

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Lewis acid catalysts. Our findings are also consistent with Travin and co-workers who report reverse Prins reaction of 3-methyl-2-buten-1-ol to form isobutylene and formaldehyde over H_2SO_4 catalyst.²⁸

The changes in carbon selectivity with time on stream for the conversion of pure 2-MTHF over SiO₂/Al₂O₃ are shown in Figure 3. The conversion based on the products formed decreases from 6.6% at 2 h to 3.8% at 6.1 h time on stream. Since the catalyst undergoes deactivation, the product selectivities at different times during the reaction can be used to understand the reaction network. The pentadiene selectivity decreases with time on stream, whereas pent-en-ol selectivity increases. Based on space time studies, pent-en-ols are primary products, and over a solid acid catalyst we anticipate the enols to undergo dehydration to produce the pentadienes; however, since the catalyst is deactivating, increasing amounts of enols are observed as the reaction progresses. It is important to note that the catalyst is continuously deactivating and the activity shown by a fresh catalyst with a high active site density may be different than the activity shown by a partially deactivated catalyst.



Figure 3. Product selectivities with time on stream for a reaction with pure 2-MTHF feed. Reaction conditions: 0.01 g SiO₂/Al₂O₃, pure 2-MTHF feed, 30 cm³ min⁻¹ He, T: 623 K; P: 1 atm.

Based on our findings, we propose a plausible reaction network for 2-MTHF ring opening as shown in Scheme 1. Attack by a proton from the silica-alumina surface can lead to the formation of a secondary carbenium ion (Scheme 1, species A) or a primary carbenium ion with a hydroxyl group attached to it (Scheme 1, species B). The majority of pentadienes are produced via the primary pathway involving concerted hydride-shift, dehydration and deprotonation. Owing to the rearrangement via hydride-shift within the carbenium intermediate, it is possible to form the diene directly without passing through either the enol or aldehyde species. We also propose a secondary pathway to pentadienes through pentanal formation based on the reactivity data obtained from reacting pentanal over SiO₂/Al₂O₃. A separate secondary pathway proceeding via pent-en-ol formation and subsequent dehydration is also possible.

In studies involving hydrodeoxygenation of 2-MTHF over metal phosphide catalysts, Oyama *et al.* used space time studies to probe the reaction network.^{20,29,30} On WP/SiO₂, the primary products were 1,4-pentadiene, *cis* and *trans*-1,3-pentadiene, and furan. The formation of pent-en-ols and butene was not observed. The authors propose that to produce pentadienes and pentanal, 2-MTHF is bound to two active sites on the catalyst. The 2-MTHF first adsorbs via the ether oxygen atom on the catalyst surface after which a surface nucleophile attacks a carbon in the alpha position to the oxygen to form a doubly bound intermediate species. In the subsequent step, the nearby vacant sites induce β -hydride elimination and release pentadienes. They also observed small amounts of pentanal formed by α -hydride elimination from the primary alkoxide species of the same doubly bound intermediate. Though the details of the mechanism outlined by

Oyama et al. and in this study are different, both mechanisms explain that dienes and aldehyde come from the same initial intermediates.

Scheme 1. Proposed reaction network for 2-MTHF ring opening to pentadiene based on space time studies over SiO₂/Al₂O₃



Effect of Temperature

Reactions were performed in the kinetically controlled regime to determine the apparent activation energy for pentadiene formation over SiO₂/Al₂O₃. Low conversion of 2-MTHF was achieved by decreasing the catalyst amount in the reactor and increasing the feed flow rate. 2-MTHF ring opening reactions were performed at four different temperatures, 573, 603, 623, and 653 K, and collected initial rate data within 10 h for each temperature. As the catalyst undergoes deactivation, the initial rate of pentadiene formation was used to determine the apparent activation energy, E_a . Figure 4 summarizes the effect of temperature on the rate of pentadiene formation. The E_a for pentadiene formation is calculated to be 74 ± 7 kJ mol⁻¹.



Figure 4. Rates of pentadiene formation at various reaction temperatures. Reaction conditions: 0.01 g SiO₂/Al₂O₃; 10 wt% 2-MTHF in dodecane, 90 cm³ min⁻¹ He, WHSV: 54 h⁻¹; P: 1 atm.

Reaction Rate Order

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The partial pressure of 2-MTHF was varied from 0.21–2.51 kPa to obtain the rate order dependence for the ring opening reaction. This variation in partial pressure was achieved by varying the 2-MTHF composition in dodecane as well as the He flow rate. A fractional rate order of 0.24 ± 0.06 with respect to 2-MTHF was obtained as shown in Figure 5. The rate of 2-MTHF consumption increases only slightly with increasing 2-MTHF concentration. This behavior can be attributed to a strong interaction between species derived from 2-MTHF and the surface of SiO₂/Al₂O₃, which is in accord with the low experimentally calculated apparent activation energy.



Figure 5. Rates of 2-MTHF ring opening over SiO_2/Al_2O_3 at various partial pressures of 2-MTHF at 623 K and 1 atm.

Catalyst Regenerability

Catalyst deactivation with time on stream was observed for all the reactions in this study due to coke formation, likely from polymerization of pentadienes. Catalyst regeneration was achieved by calcining the catalyst at 773 K (4 K min⁻¹ ramp from room temperature to 773 K, 2 h hold at 773 K) in flowing air. The CO₂ evolution was monitored during calcination using a GC-TCD. The CO₂ peak area increased with temperature and eventually decreased to zero suggesting that coke removal was complete. After calcination, reaction kinetics studies were performed with the same operating conditions. As seen in Figure 6, 2-MTHF conversion and the rate of pentadiene formation were similar for the fresh and regenerated catalyst, indicating that the deactivation is reversible. Thus, SiO₂/Al₂O₃ is regenerable upon calcination, with no observable loss in initial catalytic activity.



Figure 6. (a) 2-MTHF conversion and (b) semi-log plot of pentadiene production rate versus time on stream over fresh (\blacksquare) and regenerated (\blacksquare) SiO₂/Al₂O₃. Reaction conditions: 0.05 g SiO₂/Al₂O₃; 10 wt% 2-MTHF in dodecane feed; T: 623 K; P: 1 atm; WHSV: 11.5 h⁻¹; 90 ml min⁻¹ He. RG: Regeneration in air at 773 K for 2 h.

2-MTHF conversion over various solid acids

The conversion of 2-MTHF was further investigated over H-ZSM-5, H-MOR, H-Beta, γ -Al₂O₃, and Al-Sn-Beta. Pentadiene formation was observed over all these catalysts. No conversion of the dodecane solvent was seen during a control experiment over amorphous SiO₂/Al₂O₃ at 623 K and 1 atm. However, we observed conversion of dodecane to form aromatics compounds such as p-xylene, 1-ethyl-2-methyl-benzene, and 1,2,4-trimethyl-benzene, and cracking products, such as hexane and heptane, over H-ZSM-5. Mi and co-workers observed formation of aromatics during dodecane cracking at 673 K over H-ZSM-5.³¹ The amount of carbon present in the undesired aromatics and cracking products corresponded to approximately 10% of the total carbon detected in all the products. The formation of aromatics was not observed over γ -Al₂O₃ and the niobium-based acids. Experiments performed over Nb₂O₅ and NbOPO₄ showed pentadiene formation initially but these catalysts deactivated completely within 4 to 6 h time on stream. Both these niobium acids are white powders but upon removal from the reactor, the spent catalysts were black in color suggesting deactivation due to coke deposition.

Pentadiene formation turnover frequencies (TOF) were obtained by normalizing specific rates with the Brønsted acid site densities. The Brønsted acid site (BAS) and Lewis acid site (LAS) densities for these catalysts were taken from literature except that for SiO₂/Al₂O₃ and H-ZSM-5 which were calculated using NH₃-TPD and IPA-TPD.³² A primarily Lewis solid acid, γ -Al₂O₃, was also active for the formation of pentadiene, however, the rate was lower as compared to SiO₂/Al₂O₃. The initial rates of production of pentadiene over SiO₂/Al₂O₃ and γ -Al₂O₃ were 496 and 155 µmol g⁻¹ min⁻¹, respectively. All the catalysts underwent deactivation as the reaction progressed. The pentadiene TOF over SiO₂/Al₂O₃ decreased from 0.97 min⁻¹ to 0.45 min⁻¹ over

10 h. The initial pentadiene TOF values calculated at time zero were found to be similar for all the solid acids mentioned in Table 1. The niobium-based solid acids are not included in the table as rapid deactivation was observed within a few hours of the start of the reaction. The first order deactivation constants were calculated by plotting the semi-log plot of pentadiene formation versus time on stream. SiO₂/Al₂O₃ had the lowest deactivation constant.

Table 1. Pentadiene formation per Brønsted acid site and first order deactivation constants over

 various solid acids for 2-MTHF ring opening

| Catalyst | SiO ₂ :Al ₂ O ₃ | BAS (µmol g ⁻¹) | LAS (µmol g ⁻¹) | Pentadiene TOF (min ⁻¹) | k _d x 10 ³ (min ⁻¹) |
|-----------------|--|--------------------------------|--------------------------------|--|--|
| SiO_2/Al_2O_3 | 10.7 | 537 | 145 | 0.92 | 1.4 |
| H-ZSM-5 | 23.0 | 652 | 48 | 0.93 | 2.0 |
| H-BEA | 25.0 | 269 | 162 | 0.85 | 1.8 |
| H-MOR | 20.0 | 331 | 71 | 0.85 | 2.2 |

We compared the product selectivities over various solid acids at similar levels of conversion (~35%) in Figure 7. The highest pentadiene selectivity of ~70% was observed over SiO₂/Al₂O₃, H-ZSM-5, and Al-Sn-BEA. The other products include butene, pentanal, pent-enols, pent-en-als, and pentene. The predominantly Lewis acid catalyst, γ -Al₂O₃, had the highest butene and pent-enol selectivities. The Lewis acid site density for γ -Al₂O₃ was determined to be

 μ mol/g and no IPA decomposition to propylene was observed, indicating the absence of Brønsted acid sites. The reactors were loaded with equal amounts (0.05 g) of catalyst for SiO₂/Al₂O₃ and γ -Al₂O₃. Butene selectivities over SiO₂/Al₂O₃ and γ -Al₂O₃ are 17.5% and 21.7%, respectively. The conversion of allylic alcohol to an alkene and aldehyde (reverse Prins reaction), i.e. conversion of pent-en-ol to butene and formaldehyde in this scenario, is catalyzed by Lewis acid sites. Since γ -Al₂O₃ possesses a higher number of Lewis acid sites, a higher selectivity to butene is observed.



Figure 7. Product selectivities for 2-MTHF conversion over different catalysts at 623 K. The selectivities were compared at ~35% conversion.

Ring opening of various heterocyclics

Cyclic ethers such as tetrahydrofurans and tetrahydropyrans are other heterocyclics formed during hydrodeoxygenation of C_6 polyols.^{33,34} The ring opening of tetrahydrofuran,

tetrahydropyran, and 2,5-dimethyltetrahydrofuran was studied over SiO₂/Al₂O₃. Dehydration of THP resulted in same set of products as for 2-MTHF- pentadienes, pentenes, pentanal, pent-enols, pent-en-als, and butene. Over SiO₂/Al₂O₃, the ring opening of THF showed formation of butadiene, butanal, butenes, propene, and formaldehyde. The formation of propene and formaldehyde via reverse Prins reaction was also observed by Dauenhauer and co-workers in a recent study involving the dehydra-decyclization of tetrahydrofuran to butadiene over phosphorous self-pillared pentasil.³⁵ The formation of but-en-ol, however, was not observed. The products observed during the dehydration of 2,5-DMTHF are hexadienes, 2-hexanone, hex-enones, butenes, and acetaldehyde. The hexadiene isomers included 1,5-hexadiene, *cis* and *trans* mixtures of 1,3-hexadienes, 1,4-hexadienes, and 2,4-hexadienes. As in the case of THF, enols (hex-en-ols in the case of 2,5-DMTHF) were not seen in the product stream. The possible mechanisms for ring opening of THF and 2,5-DMTHF are shown in Scheme 2. For both THF and 2,5-DMTHF, the formation of carbonyl compounds (i.e. butanal and 2-hexanone, respectively) was observed whereas the enol species are not seen. The product selectivities for dehydration of various heterocyclics are listed in Table S2 in the Supporting Information. We speculate that the pathway for formation of the carbonyl compound is favored, as carbenium ions (Scheme 2, species D and species F) with hydroxyl group attached to the carbon bearing the positive charge are more stable than species C and E. This behavior is in agreement with work involving C-O hydrogenolysis of cyclic ethers by Chia et al. who found that the presence of hydroxyl substituent alpha to the dehydration center increases the stability of the carbenium ion.³⁶ The dehydration of THP proceeds in a pathway similar as that for THF. The rates of penten-ol formation starting from 2-MTHF and THP are 122.2 and 1.2 µmol g⁻¹ min⁻¹, respectively.

The lower specific rate for pent-en-ol formation for THP can again be explained based on the relative stability of the carbenium intermediates.

Scheme 2. Proposed mechanisms for ring opening of tetrahydrofuran (THF) and 2,5dimethyltetrahydrofuran (2,5-DMTHF) over SiO_2/Al_2O_3



As discussed earlier, the ring opening of 2-MTHF can proceed via formation of primary or secondary carbenium ions. However, for 2,5-DMTHF, the dehydration can proceed only via secondary carbenium ion formation. Dehydration for both THF and THP, which do not have the methyl branching, can proceed only by primary carbenium ion formation. The rates of ring opening of these cyclic ethers were compared by performing experiments in the differential

conversion regime for the same partial pressure of the reactant (Table 2). The flow rates of the cyclic ether and the inert carrier gas helium were adjusted to maintain the initial partial pressure at 2.4 kPa. The lowest rate of ring opening was observed for THF. Among the C_5 ethers, 2-MTHF and THP, the rate of ring opening of the former was ~92% higher. We hypothesize that the rate of 2-MTHF dehydration is higher than that of THP owing to the higher stability of secondary carbenium ion as compared to that of the primary carbenium ion. 2,5-DMTHF can undergo ring opening via two routes to form a secondary carbenium ion and thus showed the highest rate of dehydration.

| Heterocyclics | | $C_{\text{opproximation}}(0/\mathbf{)}$ | Rate of Ring Opening | |
|---------------|-----------|---|---|--|
| Structure | Name | Conversion (%) | (µmol g ⁻¹ min ⁻¹) | |
| | 2,5-DMTHF | 20.2 | 6573.7 | |
| 0 | 2-MTHF | 14.8 | 2678.6 | |
| 0 | THP | 7.3 | 1397.3 | |
| | THF | 10.1 | 1096.8 | |

Table 2. Rates of ring opening of various heterocyclics over SiO₂/Al₂O₃ at 623 K and 1 atm

The C₆ diene, *trans*-1,4-hexadiene, is used in the production of ethylene-propylene-diene monomer and is produced via ethylene and 1,3-butadiene codimerization. Behr and Miao have shown 40.3% yield to *trans*-1,4-hexadiene by the codimerization of 1,3-butadiene and ethylene in water and propylene glycol solvent over RhCl₃.³⁷ In our study, a high conversion reaction for 2,5-DMTHF showed a change in conversion from 85.4% to 75.3% over 8.3 h time on stream

(Figure 8). Throughout the reaction, a high selectivity to hexadiene isomers, particularly cis and trans 2,4-hexadiene isomers, was observed. Nearly 75% yield towards hexadienes is observed under these reactions conditions.



Figure 8. 2,5-DMTHF conversion and hexadienes yield. Reaction conditions: 0.01 g SiO₂/Al₂O₃, 5 wt% 2,5-DMTHF in dodecane, 60 cm³ min⁻¹ He, T: 623 K; WHSV: 13.3 h⁻¹; P: 1 atm.

CONCLUSIONS

We have shown that cyclic ethers can undergo ring opening to produce dienes in high yields over solid acid catalysts. Based on space time studies and changes in product distribution with time on stream, we have proposed a reaction network for 2-MTHF dehydration over SiO₂/Al₂O₃. Ring opening occurs via both a primary concerted pathway involving hydride-transfer and dehydration of a carbenium intermediate, and a secondary pathway passing through the formation of pentanal and pent-en-ols. The catalyst deactivates as the reaction progresses, but this deactivation is reversible and the initial activity of the catalyst is fully restored upon calcination in air. A fractional rate order (0.24) dependence with 2-MTHF is observed due to high surface coverage.

The apparent activation energy for 2-MTHF dehydration was calculated to be 74 kJ mol⁻¹. Other solid acids with both Brønsted and Lewis acid sites were active for the dehydration reaction to dienes with the catalytic activity for dienes formation being proportional to the concentration of Brønsted acid sites on the catalyst. Amongst the various cyclic ethers, 2,5-DMTHF showed the highest activity towards dehydration, resulting in the formation of hexadienes with ~75% yield at 623 K.

ACKNOWLEDGEMENTS

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SUPPORTING INFORMATION

Reactor schematic, verification of absence of mass transfer limitations, and product selectivities for dehydration of various heterocyclics

REFERENCES

- 1. Huber, G. W.; Iborra, S.; Corma, A. Chem. Rev. 2006, 106, 4044-4098.
- 2. Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12*, 1493-1513.

Pace, V.; Hoyos, P.; Castoldi, L.; de Maria, P. D.; Alcantara, A. R. *ChemSusChem* 2012, 5, 1369-1379.

- 4. Jessop, P. G. *Green Chem.* **2011**, *13*, 1391-1398.
- 5. Elliott, D. C.; Frye, J. G. U.S. Patent 5883266, 1999.
- 6. Xing, R.; Qi, W.; Huber, G. W. *Energy Environ. Sci.* **2011**, *4*, 2193-2205.

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Dumesic, J. A.; Alonso, D. M.; Gürbüz, E. I.; Wettstein, S. G. U.S. Patent 8399688, 2013.
 Zeitsch, K. J. *The Chemistry and Technology of Furfural and its Many by-products*. Elsevier: The Netherlands, 2000.
 Dong, F.; Zhu, Y. L.; Ding, G. Q.; Cui, J. L.; Li, X. Q.; Li, Y. W. *ChemSusChem* 2015, *8*,

1534-1537.

10. Kunkes, E. L.; Simonetti, D. A.; West, R. M.; Serrano-Ruiz, J. C.; Gartner, C. A.; Dumesic, J. A. *Science* **2008**, *322*, 417-421.

11. Blommel, P.; Dally, B.; Lyman, W.; Cortright, R. U.S. Patent 0198760, 2012.

12. Huber, G. W.; Chheda, J. N.; Barrett, C. J.; Dumesic, J. A. Science 2005, 308, 1446-1450.

13. Behr, A.; Neubert, P. ChemCatChem 2014, 6, 412-428.

14. Neubert, P.; Fuchs, S.; Behr, A. Green Chem. 2015, 17, 4045-4052.

15. Maes, M.; Alaerts, L.; Vermoortele, F.; Ameloot, R.; Couck, S.; Finsy, V.; Denayer, J. F.

M.; De Vos, D. E. J. Am. Chem. Soc. 2010, 132, 2284-2292.

16. Schniepp, L. E.; Geller, H. H. J. Am. Chem. Soc. 1945, 67, 54-56.

17. Kundu, S.; Lyons, T. W.; Brookhart, M. ACS Catal. 2013, 3, 1768-1773.

Kumar, A.; Hackenberg, J. D.; Zhuo, G.; Steffens, A. M.; Mironov, O.; Saxton, R. J.;
 Goldman, A. S. J. Mol. Catal. A-Chem. 2017, 426, 368-375.

- 19. Dumesic, J. A.; Chia, M. U.S. Patent 8404890, 2013.
- 20. Bui, P.; Cecilia, J. A.; Oyama, S. T.; Takagaki, A.; Infantes-Molina, A.; Zhao, H. Y.; Li,

D.; Rodriguez-Castellon, E.; Lopez, A. J. J. Catal. 2012, 294, 184-198.

21. Johns, I. B. U.S. Patent 2458001, 1949.

22. Norman, D. W. U.S. Patent 8981172, 2015.

23. Abdelrahman, O. A.; Park, D. S.; Vinter, K. P.; Spanjers, C. S.; Ren, L.; Cho, H. J.; Vlachos, D. G.; Fan, W.; Tsapatsis, M.; Dauenhauer, P. J. *ACS Sustain. Chem. Eng.* **2017**, *5*, 3732-3736.

24. Abdelrahman, O. A.; Park, D. S.; Vinter, K. P.; Spanjers, C. S.; Ren, L. M.; Cho, H. J.; Zhang, K. C.; Fan, W.; Tsapatsis, M.; Dauenhauer, P. J. *ACS Catal.* **2017**, *7*, 1428-1431.

25. West, R. M.; Braden, D. J.; Dumesic, J. A. J. Catal. 2009, 262, 134-143.

ACS Catalysis

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, 2009.

27. Buchanan, J. S.; Santiesteban, J. G.; Haag, W. O. J. Catal. 1996, 158, 279-287.

 Ryabova, R. S.; Osipova, G. F.; Travin, S. O. Russian Chemical Bulletin 1995, 44, 840-843.

29. Bui, P. P.; Oyama, S. T.; Takagaki, A.; Carrow, B. P.; Nozaki, K. ACS Catal. 2016, 6, 4549-4558.

30. Iino, A.; Cho, A.; Takagaki, A.; Kikuchi, R.; Oyama, S. T. J. Catal. 2014, 311, 17-27.

31. Xian, X. C.; Liu, G. Z.; Zhang, X. W.; Wang, L.; Mi, Z. T. Chemical Engineering Science 2010, 65, 5588-5604.

32. Kubicka, D.; Kumar, N.; Maki-Arvela, P.; Tiitta, M.; Niemi, V.; Karhu, H.; Sami, T.; Murzin, D. Y. *J. Catal.* **2004**, *227*, 313-327.

33. Kim, Y. T.; Dumesic, J. A.; Huber, G. W. J. Catal. 2013, 304, 72-85.

34. West, R. M.; Kunkes, E. L.; Simonetti, D. A.; Dumesic, J. A. *Catal. Today* **2009**, *147*, 115-125.

35. Abdelrahman, O. A.; Park, D. S.; Vinter, K. P.; Spanjers, C. S.; Ren, L.; Cho, H. J.; Vlachos, D. G.; Fan, W.; Tsapatsis, M.; Dauenhauer, P. J. *ACS Sustain. Chem. Eng.* **2017**.

36. Chia, M.; Pagan-Torres, Y. J.; Hibbitts, D.; Tan, Q. H.; Pham, H. N.; Datye, A. K.; Neurock, M.; Davis, R. J.; Dumesic, J. A. J. Am. Chem. Soc. **2011**, *133*, 12675-12689.

37. Behr, A.; Miao, Q. Green Chem. 2005, 7, 617-620.

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82x34mm (300 x 300 DPI)



Figure 1 99x78mm (300 x 300 DPI)



















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Figure 5

100x79mm (300 x 300 DPI)

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Figure 7 88x61mm (300 x 300 DPI)

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Pentadienes

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Page 43 of 43

