

DEHYDRA-DECYCLIZATION OF CYCLIC ETHERS FOR RENEWABLE RUBBER MONOMERS

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Abstract

The catalytic synthesis of on-purpose dienes including butadiene and isoprene occurs through the selective ring-opening dehydration of cyclic ethers such as tetrahydrofuran and 3-methyl-tetrahydrofuran. Solid acid catalysts including H-ZSM5 and variants thereof exhibit high activity but limited selectivity for dienes, while weaker solid acid catalysts comprised of microporous supports and impregnated weak active sites achieve selectivity >90% to dienes such as butadiene. The mechanisms and kinetics of the competing pathways to butadiene are described, and key side reactions to retro-Prins products are characterized and related to the design of microporous catalytic systems.

Keywords

Butadiene, Isoprene, Zeolite, Dehydration

Introduction

The synthesis of butadiene and isoprene from renewable sugars requires the elimination of oxygen and the conversion of five- or six-carbon sugars to five- or four-carbon dienes. This transformation can occur by catalytic dehydration, which removes water to produce an olefin with comparable overall carbon oxidation state. Production of dienes from oxygenates has been evaluated for decades, with molecules such as 1,4-butanediol, 1,3-butanediol, and 2,3-butanediol serving as biomass-derived feedstock for butadiene (Makshina, et al. 2014).

In this work, we evaluate the conversion of cyclic ethers including tetrahydrofuran, 2-methyl-tetrahydrofuran and 3-methyl-tetrahydrofuran to butadiene, pentadiene, and isoprene, respectively. (Abdelrahman, et al. 2017a, 2017b) While THF-containing molecules with linear carbon chains can be obtained from furfural via hydrogenation and/or decarbonylation, 3-methyl-THF with a branched carbon backbone is obtained in a hybrid process (Schmidt &

Dauenhauer, 2007) from mesaconic acid (Park, et al. 2018). In this work, ring-opening dehydration of these cyclic ethers is examined using a range of strong and weak solid acid catalysts within microporous reaction environments to understand catalyst and reactor design for optimal yield of dienes.

Results

As depicted in Figure 1, dehydra-decyclization of THF and was evaluated in a continuous flow packed-bed reactor of various solid acid catalysts including phosphorous-containing siliceous self-pillared pentasil (P-SPP), H-Y, HZSM-5, silica-alumina, niobium oxide, Sn-BEA, zirconia, and phospho-tungstic acid (PWA).

As shown, the varying catalysts exhibited dramatically different yields and conversions of tetrahydrofuran to butadiene. Strong acids such as H-Y and HZSM-5 were the

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most active, but they were particularly unselective ($5\% < S < 25\%$). Silica alumina was more active and selective ($40\% < S < 75\%$). However, all-silica supports impregnated with phosphoric acid and calcined such as P-SPP were highly selective for butadiene ($85\% < S < 97\%$), even at conversions as high as 90%.

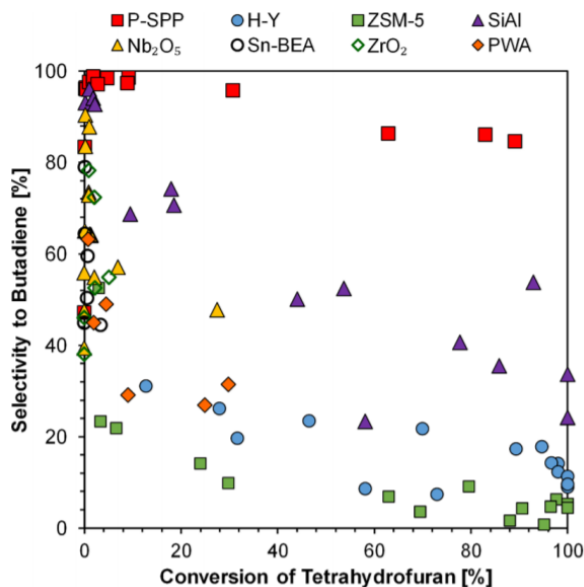


Figure 1. Dehydra-decyclization of tetrahydrofuran to butadiene. Vapor-phase reactions evaluated by the microcatalytic method at 200–400 °C and space velocities of 1–90 s⁻¹ with solid acid catalysts: Phosphorus self-pillared pentasil (P-SPP, red ■), faujasite (H-Y, blue ●), ZSM-5 (green ■), silica–alumina (SiAl, purple ▲), niobium oxide (Nb₂O₅, yellow ▲), Sn-BEA (○), zirconium oxide (ZrO₂, ◇), phosphotungstic acid (PWA, orange ◆).

The conversion of THF was examined to determine the mechanism, rate-limiting step, and role of confining structure on the activity and selectivity to butadiene. The apparent activation energy and the low rate dependence on the reactant ether both indicated the importance of catalytic opening of the ring on the overall performance of the reaction. Kinetic isotope studies indicate that the degree of rate control can be attributed primarily to a single step. This conclusion is further evaluated in alkylated THF feedstocks, where the relative rates of tandem kinetics are different due to faster ring-opening of the cyclic ether. The measured experimental kinetics were combined with a microkinetic model comprised of computed energies of five parallel pathways, and the primary pathway was identified as consistent with all experimental evidence.

Conclusions

The dehydra-decyclization of THF and methylated THF produces butadiene, pentadiene, and isoprene at high yield using weak solid acids such as phosphorous-containing all-silica zeolites. The mechanism leading to a high yield of dienes was identified as a tandem system of

both ring-opening and immediate dehydration, thereby limiting the potential for intermediate chemistries. The extent of side products were attributed to catalytic retro-prins chemistries. All pathways were identified and evaluated using experimental kinetics in combination with a microkinetic model comprised of computed kinetics.

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