Conversion of butanol to propene in flow: a triple dehydration, isomerisation and metathesis cascade

Supporting Information

Yiping Shi,[1,*] Andrew S. Weller,[2] A. John Blacker,[3] Philip W. Dyer[1,*]

[1]Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK
[2]Department of Chemistry, University of York, University of, York YO10 5DD, UK
[3]School of Chemistry, University of Leeds, Woodhouse, Leeds LS2 9JT, UK

1. Indiviudal reactor schematics for cascade Steps 1-3

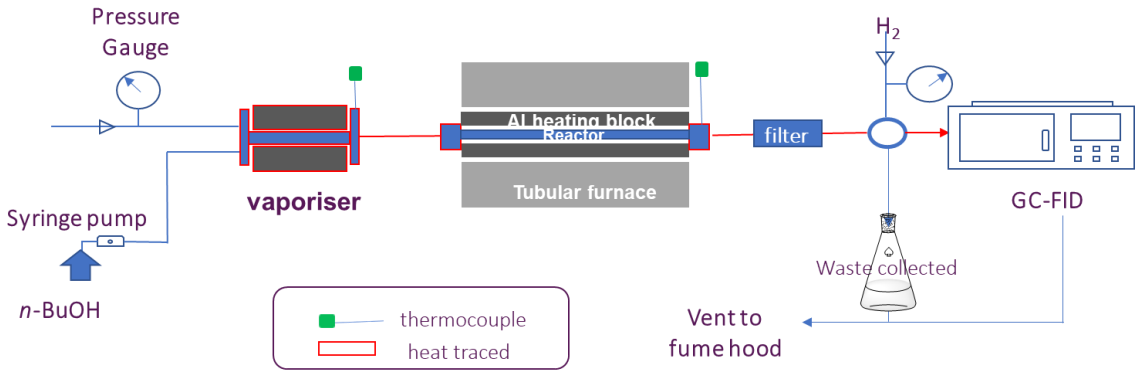

Figure S1. Reactor scheme for *n*-BuOH dehydration.

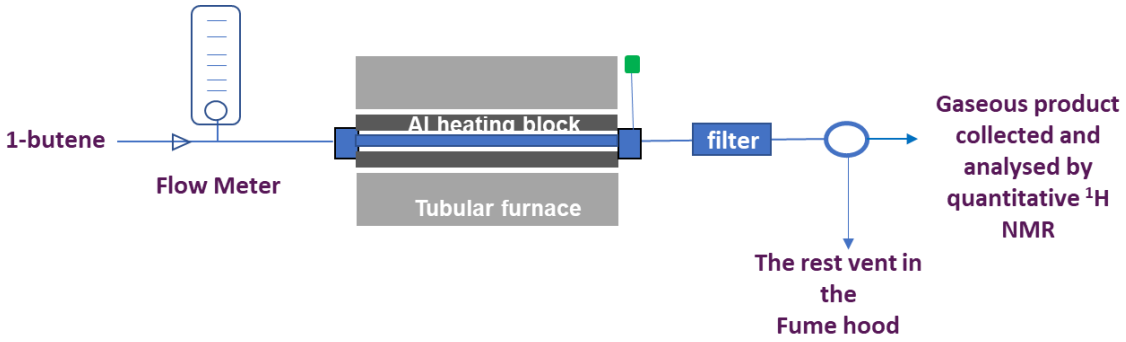

Figure S2. Reactor scheme for butenes isomerisation.

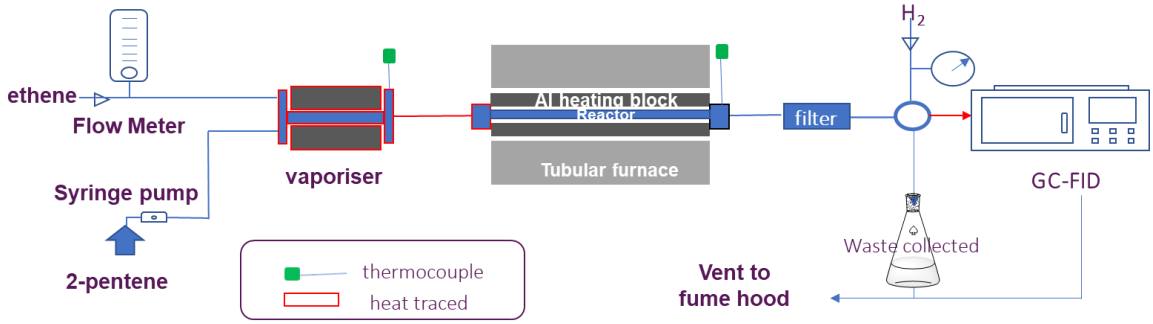

Figure S3. Reactor scheme for the cross-metathesis of ethene with 2-pentenes.

The triple cascade reactor schematic is presented in the body of the mauscript.

2. Dehydration of butanol with H-ZSM-5 for over 70 hours

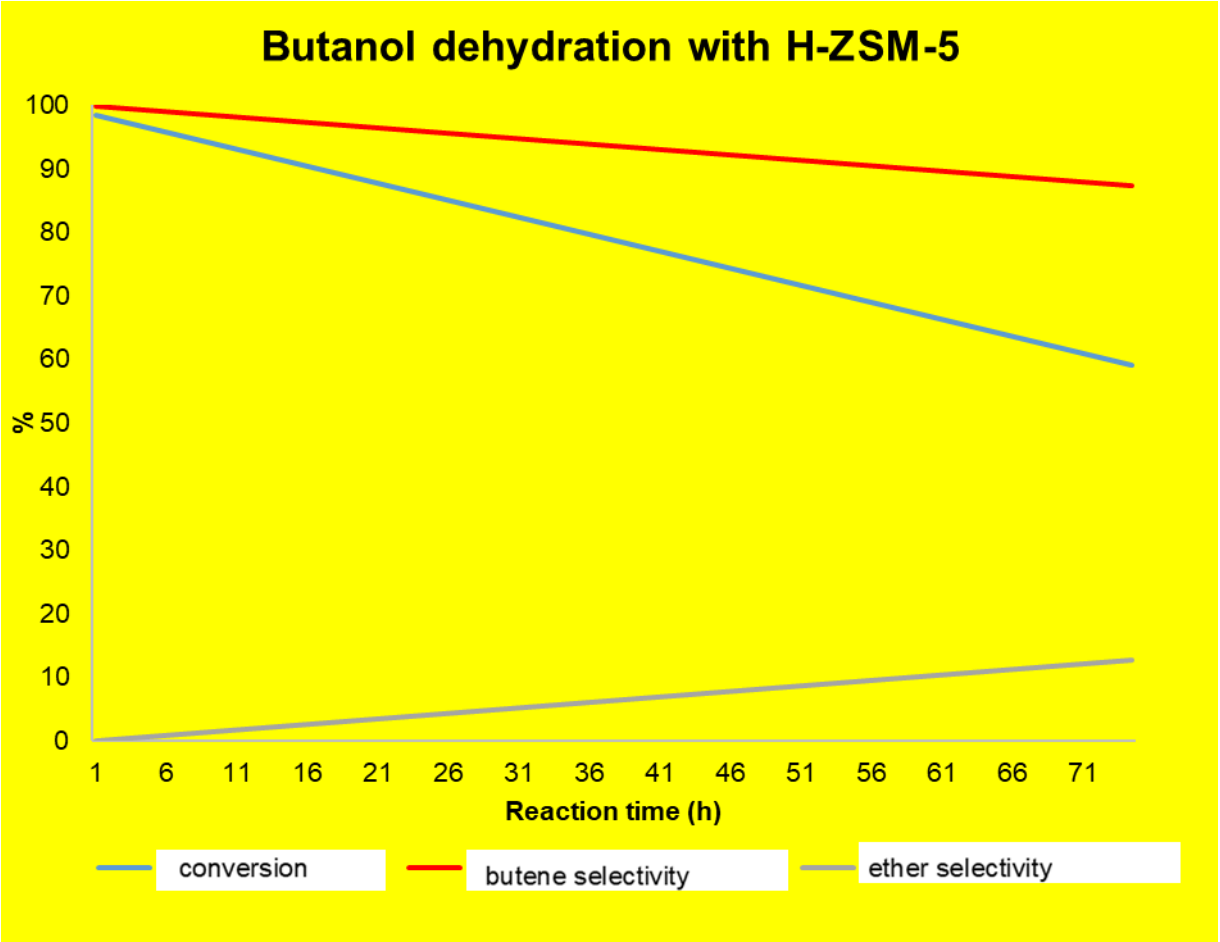

Figure S4. Conversion of *n*-butanol to butene with H-ZSM-5 at 250 °C, 0.024 mL min^{-1} flow rate for over 70 hours on stream.

For butanol dehydration, conversion was calculated as:

$$\left(\frac{butanol\ before\ dehydration - butanol\ after\ dehydration}{butanol\ before\ dehydration}\right) * 100$$

The selectivity of butenes was calculated by:

$$\left(\frac{no.moles\ of\ butenes}{no.of\ moles\ of\ butenes + no.of\ moles\ of\ di-n-butyl\ ether}\right) * 100$$

3. Representative GC-FID chromotogram for *n*-BuOH dehydration

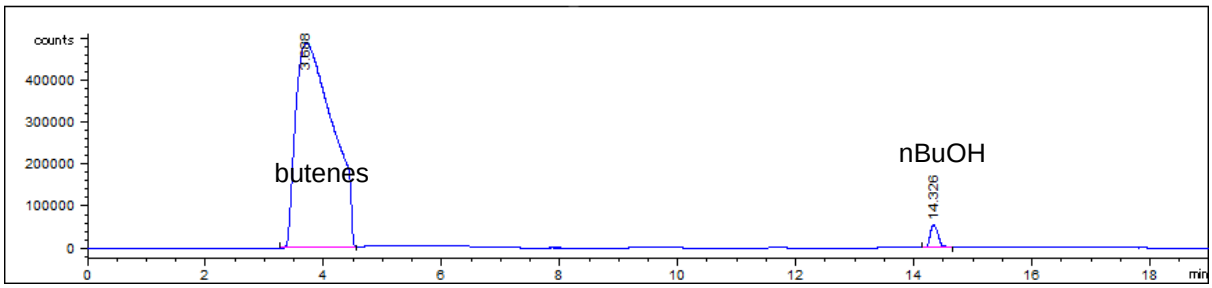

Figure S5. GC-FID chromatogram of *n*-BuOH dehydration over H-ZSM-5 at 250 °C with 0.024 mL min^{-1}.

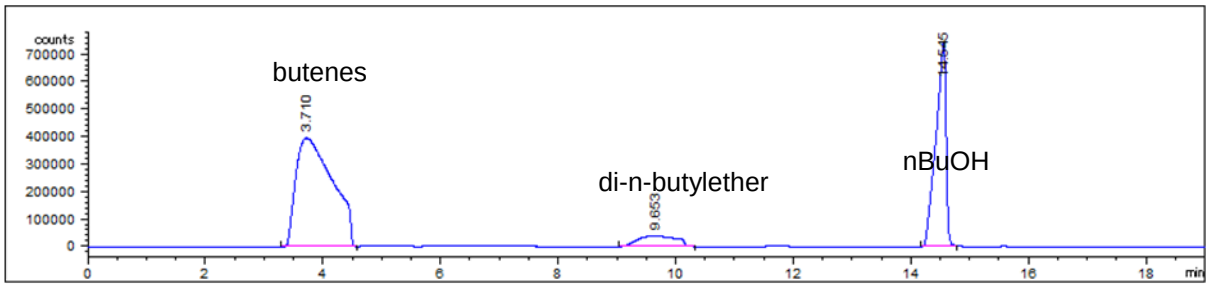

Figure S6. GC-FID chromatogram of *n*-BuOH dehydration over H-ZSM-5 at 250 °C with 0.024 mL min^{-1} after 50 hours.

4. Quantitative ^{1}H NMR spectroscopic analysis of 1-butene isomerisation

For the isomerisation of 1-butene, the conversion was calculated as $\left(1-\frac{no.moles\ of\ 1-butene}{no.moles\ of\ all\ the\ butene\ isomers}\right)*100$

The selectivity of butene isomers was calculated as $\left(\frac{no.\ moles\ certain\ butene\ isomer}{no.\ molesof\ cis-2-butene+trans-2-butene+isobutene}\right)*100$

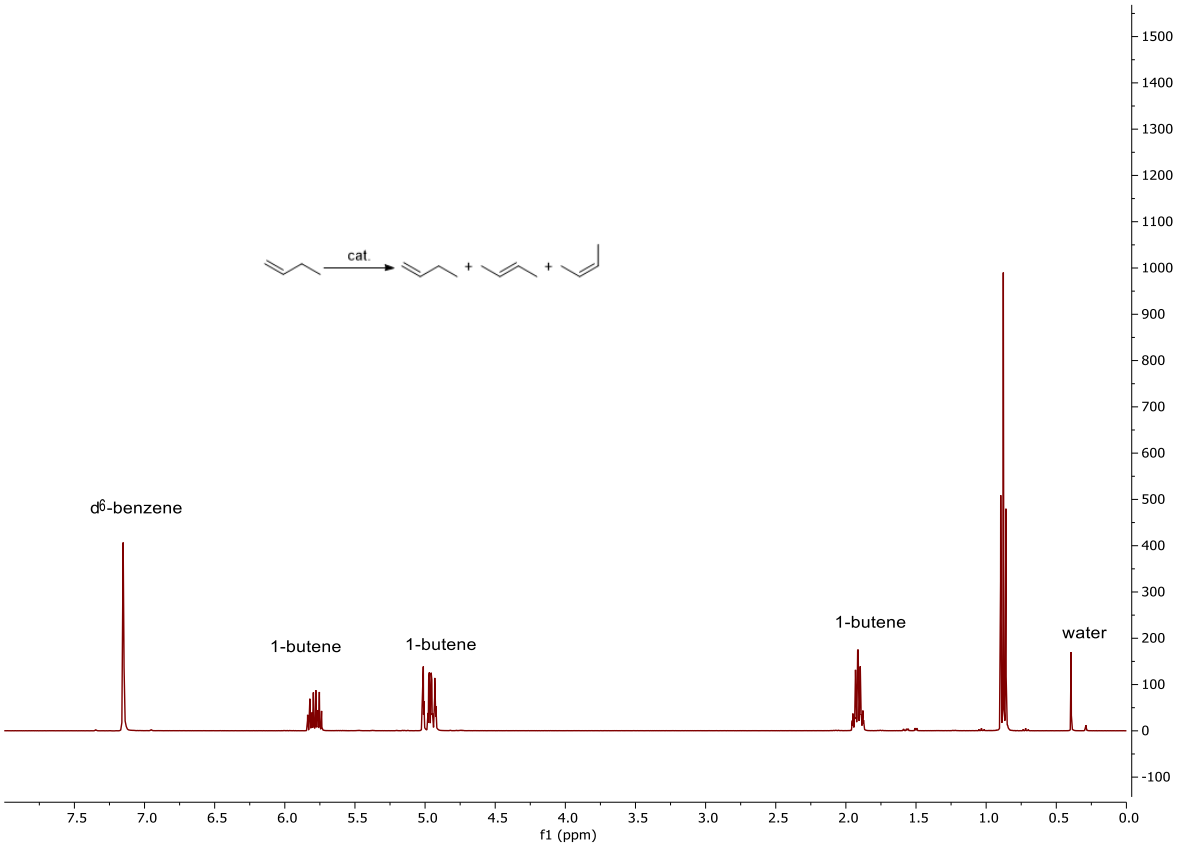

Figure S7. ^{1}H NMR (400 MHz, C_6D_6) spectrum of 1-butene isomerisation over H-Fer at 25 °C

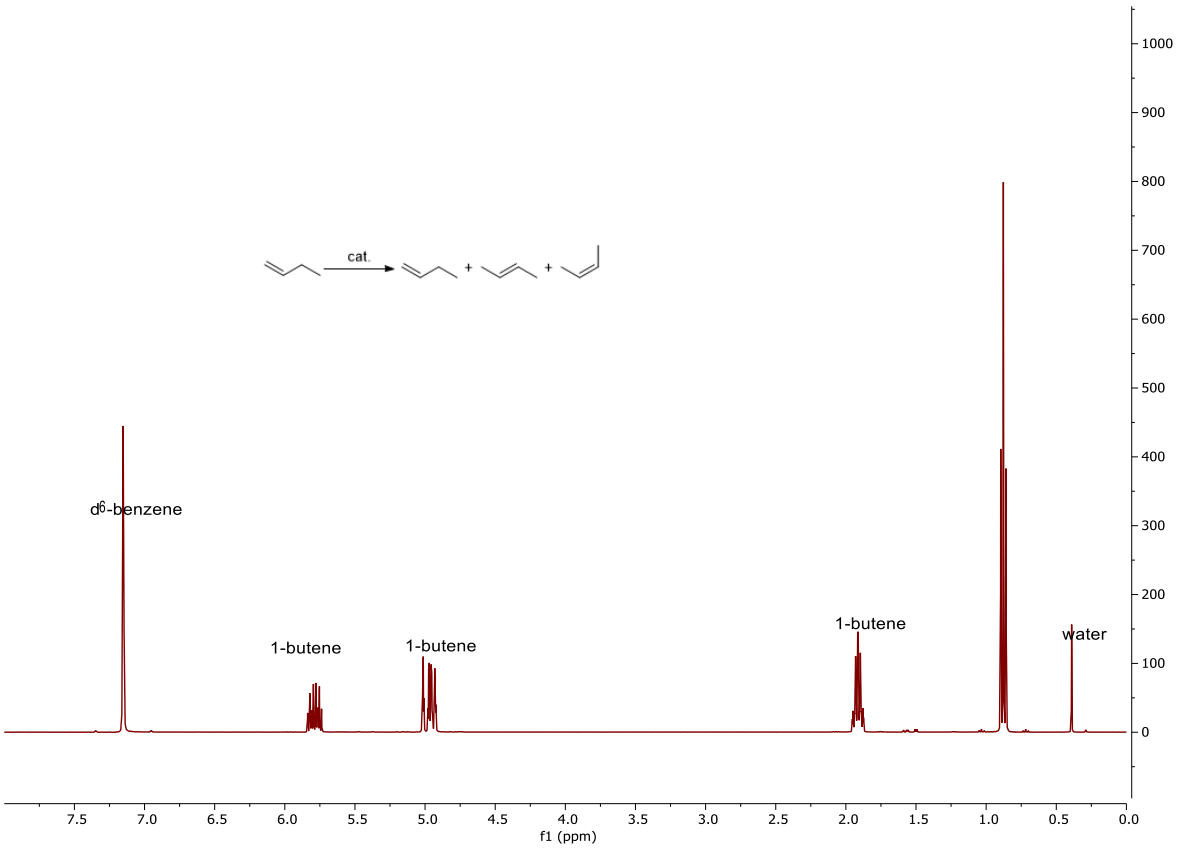

Figure S8. ^{1}H NMR (400 MHz, C_6D_6) spectrum of 1-butene isomerisation over H-Fer at 50 °C

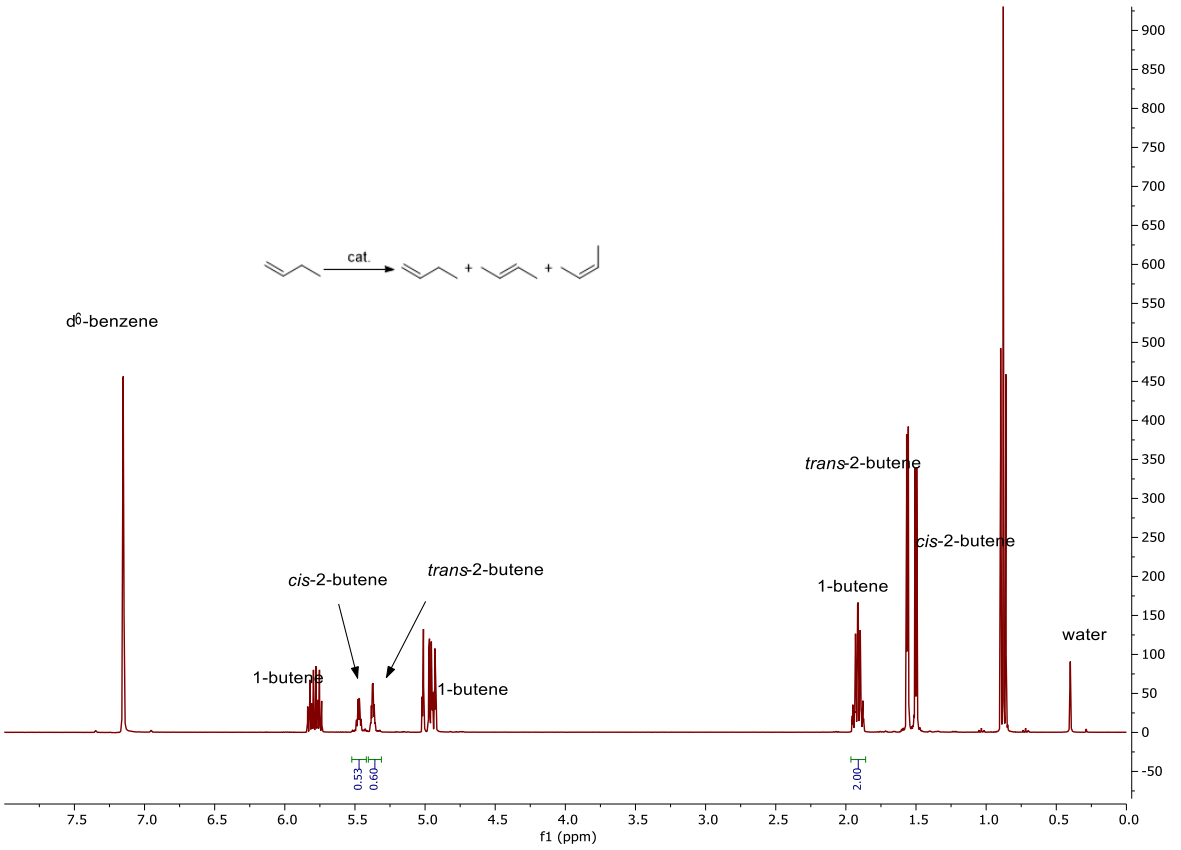

Figure S9. ^{1}H NMR (400 MHz, C_6D_6) spectrum of 1-butene isomerisation over H-Fer at 100 °C

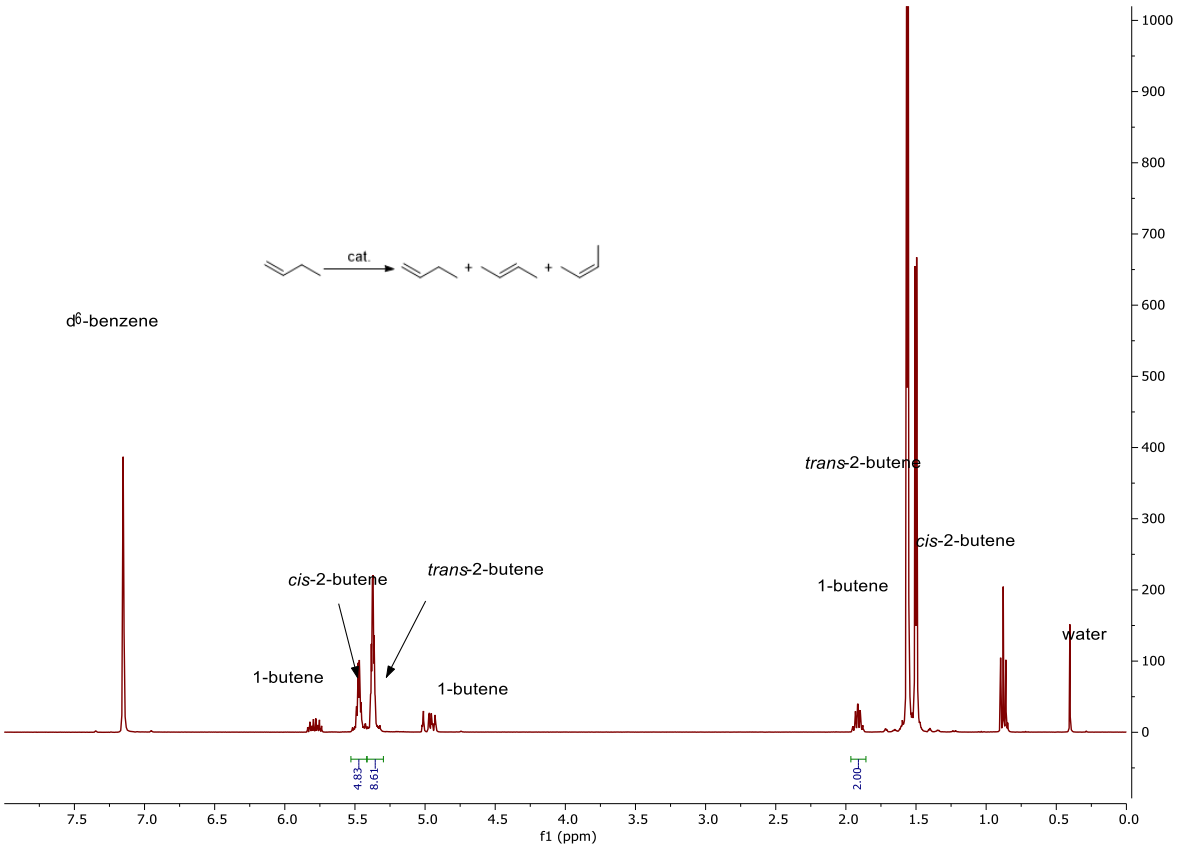

Figure S10. ^{1}H NMR (400 MHz, C_6D_6) spectrum of 1-butene isomerisation over H-Fer at 150 °C

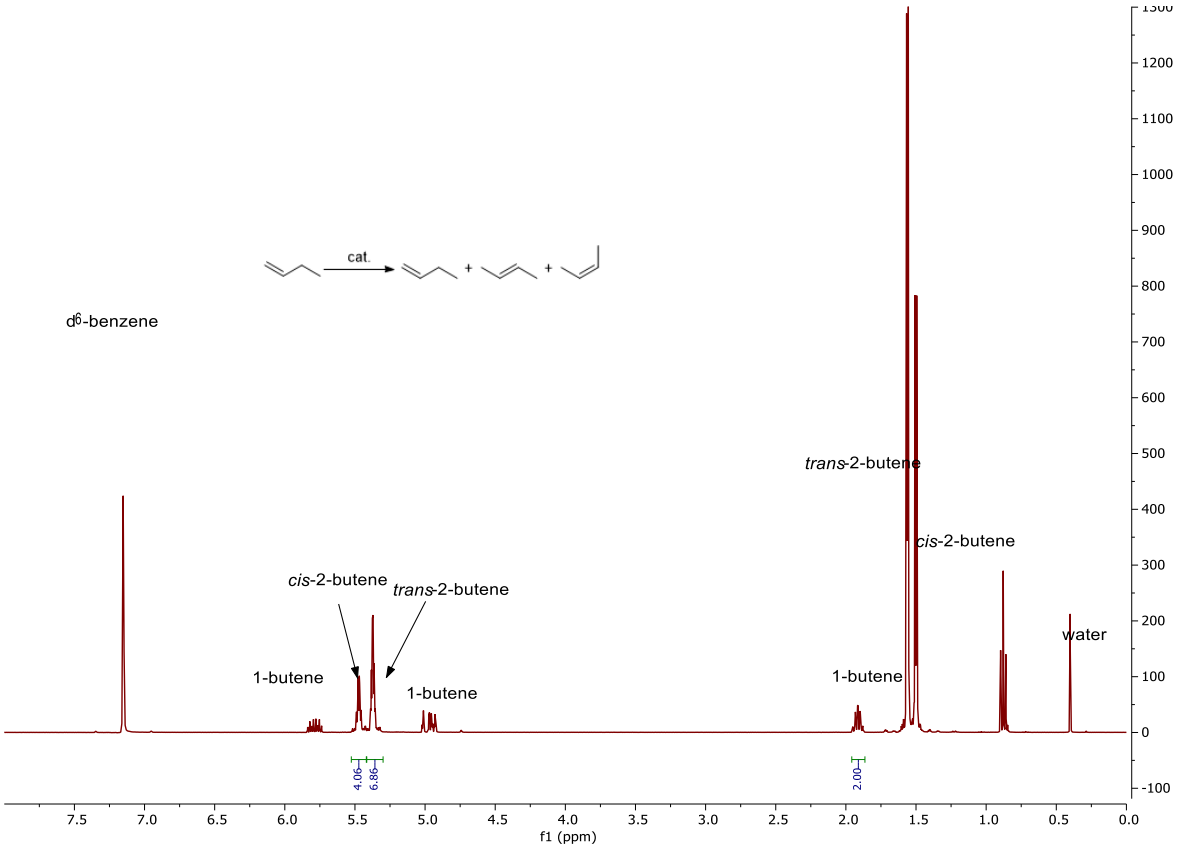

Figure S11. ^{1}H NMR (400 MHz, C_6D_6) spectrum of 1-butene isomerisation over H-Fer at 200 °C

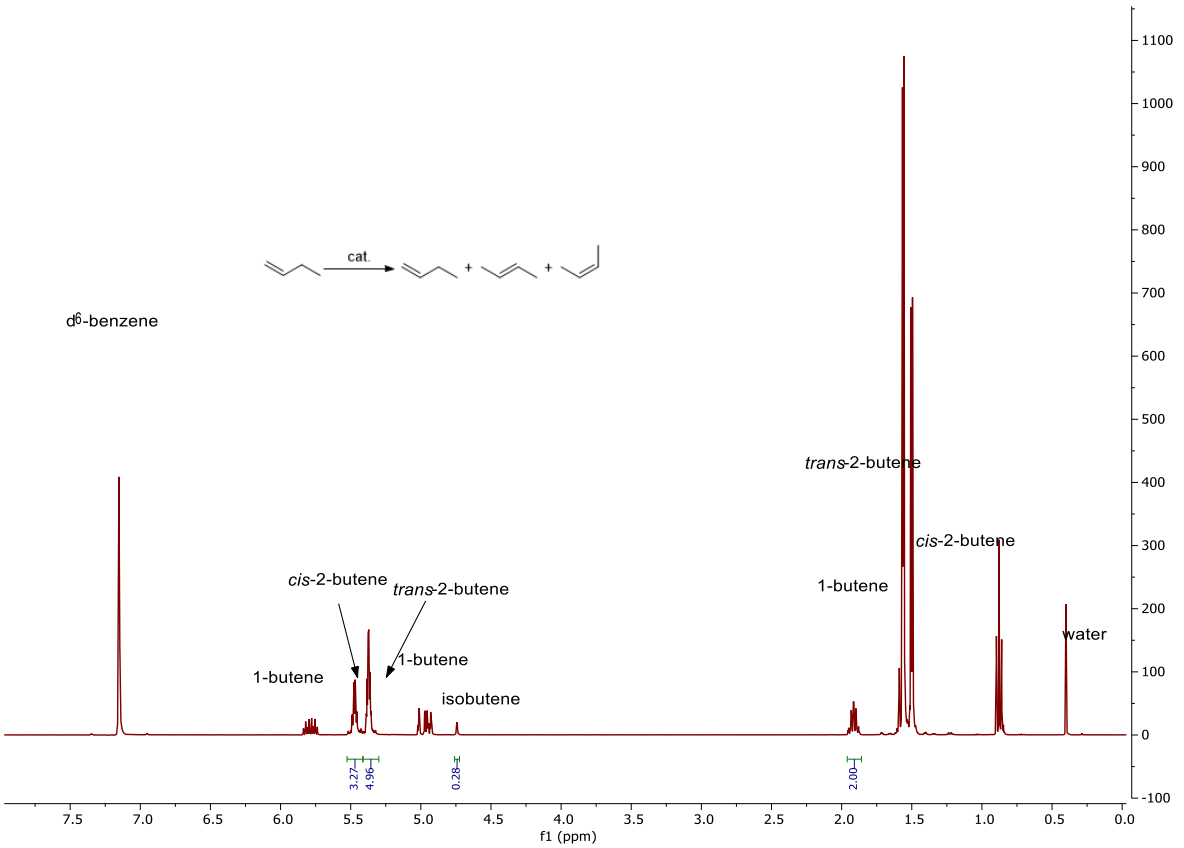

Figure S12. ^{1}H NMR (400 MHz, C_6D_6) spectrum of 1-butene isomerisation over H-Fer at 250 °C

5. Quantification of conversion and selectivity for 2-pentene/ethene cross-metathesis

The metathesis activity was measured over one hour on stream for each catalyst. The conversion and selectivity were calculated based on the metathesis products. Calculations used to determine 2-pentene and butenes conversion, and butene and propebe selectivity are given below.

The metathesis activity was measured over one hour on stream for each catalyst. The conversion and selectivity were calculated based on the metathesis products. For the metathesis of 2-pentene, the conversion was calculated as $(1 - \frac{no.moles\ of\ 2{-}pentene}{no.moles\ of\ 2{-}pentene + all\ products}) * 100$

The selectivity of butenes was calculated as $\left(\frac{no.moles\ of\ butenes}{no.moles\ of\ all\ products}\right) * 100$

For the metathesis of butenes, the conversion was calculated as $(1 - \frac{no.moles\ of\ butenes}{no.moles\ of\ butenes + all\ products}) * 100$

The selectivity of propene was calculated as $(\frac{no.moles\ of\ propene}{no.moles\ of\ all\ products}) * 100$

6. Representative GC-FID chromatogram of 2-pentene/ethene cross-metathesis

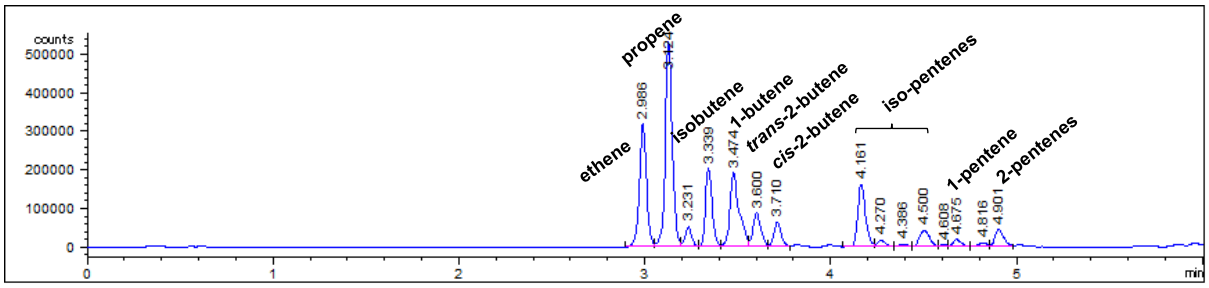

Figure S13. GC-FID chromatogram of 2-pentene/ethene (ratio 1:1) cross-metathesis over W on acid-washed SiO_2/Al_2O_3 at 500 °C.

7. Representative GC-FID chromatagram of direct triple cascade conversion of *n*-BuOH to propene in flow

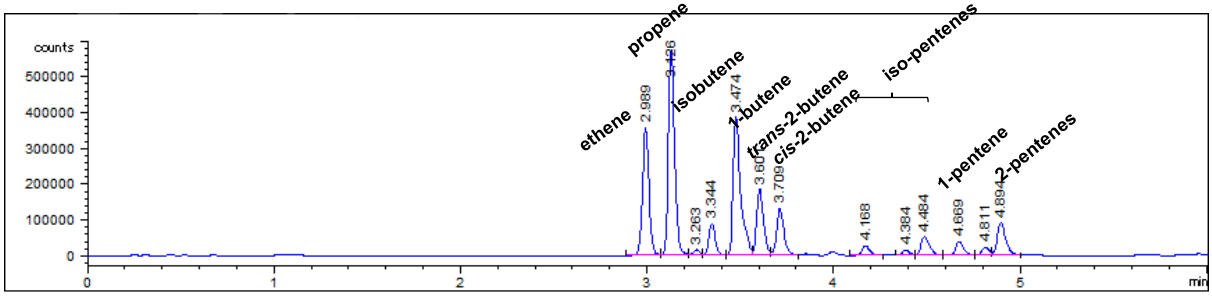

Figure S14. GC-FID chromatogram of *n*-BuOH conversion to propene in a single three-step flow cascade as measured at the outlet of reactor 3.

8. GC quantification for the metathesis step

GC quantification for both starting materials and products for the metathesis step were calculated relative to 2-butene using previously reported Thermal Response Factors.[1] Thermal response of reagents and products are shown in Table S1.

Table S1. Calculated relative response factors for the starting materials and products of the metathesis step.

	Thermal response	R_f relative to 2-butene
2-butene	86	1
propene	64.5	0.75
1-butene	81	0.94
iso-butene	82	0.95
1-pentene	98.5	1.15
iso-pentene	99	1.15
trans-2-pentene	104	1.21
cis-2-pentene	98.5	1.15
hexene	123	1.43

[1] W.A. Dietz, Response factors for gas chromatographic analyses, J. Chromatogr. Sci. 5 (1967) 68–71. https://doi.org/10.1093/chromsci/5.2.68.