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

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Abstract

A combined three-step flow cascade conversion of *n*-butanol to propene is demonstrated. Zeolite H-ZSM-5 gives high conversion in the initial *n*-butanol dehydration step (98%). Subsequent isomerisation of terminal butenes to internal butenes over zeolite H-Fer takes place with good conversion (87%). Finally, cross-metathesis with ethene over a tungsten on acid-washed SiO_2/Al_2O_3 catalyst affords propene with good selectivity (65%). Coupling these three steps into a single flow sheet gives an overall yield of 64% propene from *n*-BuOH. Ethene cross-metathesis catalyst performance was probed using 2-pentene as a model co-substrate giving good conversion (~90%) and moderate selectivity to butenes (67%).

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Key words: Butanol, propene, dehydration, isomerisation, cross metathesis, flow

1. Introduction

Industrially, propene is an important building block for the preparation of a wide range of chemicals and is the second most used petrochemical feedstock after ethene.[1] Although the largest market for propene is in the manufacture of polypropene (~70%), the synthesis of propenoic acid, propenonitrile, epoxypropane, (1-methylethyl)benzene, and epoxypropane also consume significant quantities. Traditionally, propene has been produced as a by-product from steam cracking [2] and fluid catalytic cracking.[3] However, the emergence of shale gas resources over the last decade has driven conversion of many cracking units to use ethane as a feed rather than naphtha,[4] which has resulted in a very considerable shift of the product slate away from propene to predominantly ethene. Consequently, the supply of propene cannot keep pace with increasing demand (expected to be 135 million tonnes in 2025 [5]), which has made the development of on-purpose propene (OPP) production processes of increasing interest.[5] Today, the three most widely investigated OPP processes are catalytic propane dehydrogenation, the methanol to olefins (MTO) process, and cross-metathesis of ethene with butenes, few of which have reached full commercialisation to date.[6]

In parallel, attention is focussing increasingly on more sustainable routes for olefin production, with dehydration of bio-derived ethanol and butanol to ethene and butenes, respectively, being at the forefront of this area.[7] Today there is growing availability of bio-derived butanol, with an estimate of over 247 billion tonnes being produced annually worldwide.[8] Notably, the availability of bio-derived alcohols continues to increase as a result of implementation of processes such as ABE fermentation, which gives a mixture of acetone, butanol and ethanol. However, currently, there are few OPP routes to propene from sustainable feedstocks. For example, a two-stage process has been developed for the production of propene through glycerol hydrogenolysis and subsequent dehydration,[9] although a costly iridium-based catalyst is required. The work described in this communication describes a flow triple cascade process that converts *n*-butanol to propene in an integrated fashion. This offers future opportunities for bio-derived propene manufacture.

2. Experimental

Zeolite ferrierite (SAR 20), zeolite beta (SAR 25), zeolite ZSM-5 (SAR 23), zeolite-Y (SAR 80) each as their ammonium forms; ammonium tungsten oxide hydrate; and ammonium molybdate (*para*) tetrahydrate (99%) were purchased from Alfa Aesar. SiO_2 gel, SiO_2/Al_2O_3 support, 1-butene (>99%) and γ-Al_2O_3 were obtained from Sigma Aldrich (Merck). 2-Pentene (*cis*- and *trans*-mixture, >95%) and MgO were sourced from Fluorochem. Ethene (99.9%) was purchased from BOC and was used as received.

Prior to catalysis, the ammonium forms of the zeolites ZSM-5 (SAR 23), ferrierite (SAR 20), Y (SAR 80) and beta (SAR 25) were converted to their corresponding protic forms, H-ZSM-5, H-Fer, H-Y and H-Beta by calcination under static air (NH_4-ZSM-5: heated to 500 °C at 10 °C min^{-1} and held for 4 hour; NH_4-Fer and NH_4-Y: heated to 550 °C at 2 °C min^{-1} and held for 5 hours; NH_4-Beta: heated to 2 °C min^{-1} to 500 °C and held for 5 hours) and then allowed to cool slowly to room temperature before being stored in sealed vials. Before testing, the zeolites (as their acid forms) were pressed into pellets by application of 10 tons pressure for 30 seconds, and then crushed and sieved to 250-500 microns.

2.1. Catalytic Alcohol Dehydration

A ¼'' o.d. stainless steel reactor tube was charged with quartz wool (30 mg), pressed, crushed, and sieved zeolite catalyst {acid form} (0.1 g), and finally more quartz wool (30 mg). Testing was done by first heating the catalyst at 150 °C under N_2 for 1 h (N_2 flow rate 30 mL min^{-1}) and then heating the reactor tube to the desired reaction temperature (250 °C) before *n*-butanol was allowed to flow through the catalyst bed using a syringe pump (0.024 mL min^{-1}) after initially passing through a vaporiser unit held at 155 °C. The system is heat traced at 155 °C to ensure substrate and products remain in the gaseous phase. Product analysis for the dehydration step was performed using an on-line GC-FID system (HP5890-II) employing a Stabilwax-DA column (30 m length, 0.25 mm i.d., 0.20 μm film thickness) using the following heating profile: column held at 40 °C for 10 mins prior to and ramping at 30 °C min^{-1} to 220 °C where the temperature was held for 3 mins. GC calibration curves for starting materials and products were established using nonane as internal standard. Response factor (R_f) of 1-butene is 0.46, and R_f of di-*n*-butyl ether is 0.78. Calculations used to determine butanol conversion by dehydration and for the butene selectivity are given in the SI.

2.2. Olefin Isomerisation Catalysis

A ¼'' o.d. stainless steel reactor tube was charged with quartz wool (30 mg), pressed, crushed, and sieved catalyst (0.1 or 0.2 g), and more quartz wool (30 mg). Testing was done by first heating the catalyst at 150 °C under N_2 for 1 h (N_2 flow rate 30 ml min^{-1}), which was then cooled or heated to the desired reaction temperature (20 - 250 °C) before a flow of 1-butene (6 mL min^{-1}) was passed through the heated catalyst bed. The gaseous products were collected in a gas sampling balloon attached to the outlet tube; the gaseous products were then bubbled slowly *via* a needle through deuterated benzene (0.7 mL) in an NMR tube, which was quickly sealed and thoroughly shaken, and the resulting solution analysed by ^1H NMR spectroscopy (Bruker Advance spectrometer, 400 MHz). Calculations used to determine 1-butene conversion and butene selectivity are given in the SI.

2.3 Catalytic Olefin Cross-Metathesis

2.3.1. Catalyst preparation: incipient wetness impregnation

The catalysts, Mo on SiO_2/Al_2O_3, Mo on SiO_2, Mo on H-Y/γ-Al_2O_3, were prepared by incipient wetness impregnation using a modification of a literature procedure.[10] The SiO_2/Al_2O_3, SiO_2 and H-Y/γ-Al_2O_3 supports were dried at 110 °C for 16 hours, then calcined at 500 °C for 5 hours (2 °C min^{-1} heating ramp rate) under static air before being allowed to cool slowly to room temperature. The desired amount of ammonium molybdate tetrahydrate was dissolved in a minimum amount of deionised water (based on support pore volumes): 2.6 mL for SiO_2/Al_2O_3; 5.6 mL for SiO_2; 2.0 mL for H-Y/γ-Al_2O_3. The calcined support was then impregnated by dropwise addition of an aqueous solution of ammonium molybdate tetrahydrate. The resulting materials were then first dried at 110 °C in an oven for 16 hours under static air, then subsequently calcined at 400 °C for 2 h (heating rate 1 °C min^{-1}), before being finally allowed to cool slowly to room temperature. All the catalysts were pressed at 10 tons for 30 seconds before being crushed and sieved to 250-500 microns.

2.3.2. Catalyst preparation: aqueous impregnation

The materials W on SiO_2/Al_2O_3, Mo on acid washed SiO_2/Al_2O_3, W on acid-washed SiO_2/Al_2O_3, W on SBA-15 were prepared by aqueous impregnation using a modification of a literature procedure.[11] In each case, the desired support was first calcined (500 °C, 15 hours, 5°C min^{-1} heating rate) under static air and allowed to cool slowly to room temperature. Solutions of ammonium molybdate or ammonium tungsten oxide in deionised water were prepared (6.66 g metal per litre, 0.0054 M). The metal-containing catalyst precursor solution (48 mL) was added to a suspension (4 g) of previously-calcined support in deionised water (152 mL) and stirred for 2 hours with a magnetic stirrer bar. Water was evaporated using a rotary evaporator at 60 °C, 160 mbar. The resulting solid was dried in an oven under static air at 110 °C overnight, before finally being calcined at 500 °C for 2 hours (heating ramp rate 5 °C min^{-1}) and allowed to cool slowly to room temperature. Samples of each of the catalysts were then pressed at 10 tons for 30 seconds before being crushed and sieved to 250-500 microns.

2.3.3. Catalyst preparation: acid-washed SiO_2/Al_2O_3 support

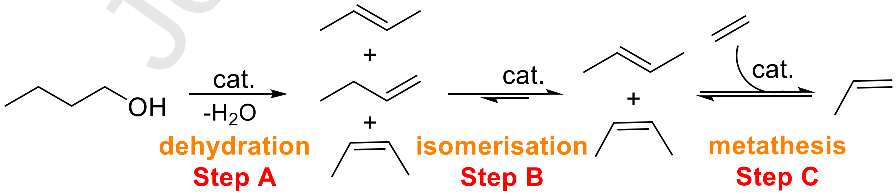
A round bottomed flask was charged with SiO_2/Al_2O_3 (20 g) and then aqueous HNO_3 (0.05 M, 200 mL) added. The resulting suspension was then heated at 80 °C for 1 hour in an oil bath. After cooling, the acid-modified SiO_2/Al_2O_3 was then washed with deionised water (200 mL) using a Buchner filter, before the washed material was dried at 110 °C in an oven under static air overnight. The whole acid wash/water wash process was then repeated a further two times; the resulting material was then used to prepare the metathesis catalysts.

2.3.4. Catalysis

A ¼'' diameter stainless steel reactor tube was charged with quartz wool (30 mg), pressed, crushed, and sieved catalyst (0.2 g) and then more quartz wool (30 mg). Testing was done by first heating the catalyst at 550 °C (heating rate 5 °C min^{-1}) under N_2 (flow rate 3 mL min^{-1}) for 2 h and then allowed to cool to the desired temperature (40 - 550 °C) at which point the olefin was admitted to the system and allowed to contact the catalyst. When liquid 2-pentene was used as feed, this was added *via* a syringe pump and vaporiser, while gaseous ethene was introduced directly into the reactor system *via* a non-return valve with its flow rate controlled by a gas flow meter. The composition of the products produced was analysed on-line using an HP 5890-II GC-FID. The separation of hydrocarbons was performed on an HP-PONA column (50 m length, 0.2 mm i.d., 0.5 μm film thickness), with the temperature held constant at 30 °C for 10 mins. 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 propene selectivity are given in the SI.

3. Results and Discussion

A three-step triple cascade system has been developed to convert butanol to propene in flow. The cascade combines *n*-butanol dehydration to butenes (Step A), isomerisation of 1-butene to 2-butenes (Step B), and cross-metathesis of 2-butenes with ethene to afford propene (Step C), as illustrated in Scheme 1. The development of each of these catalytic processes will be considered in turn.

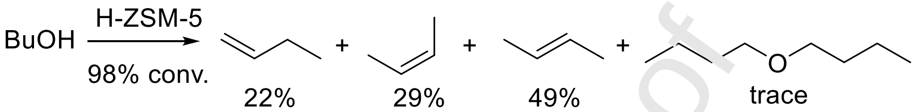


Scheme 1. Conversion of *n*-butanol to propene in a three-step cascade.

3.1. Dehydration of *n*-butanol

Industrially, 1-butene is produced principally by two methods. Fractional distillation from a crude C_4 refinery steam, which yields a mixture of 1- and 2-butenes [12] and dimerisation of ethene to yield 1-butene directly.[13] More recently, attention has turned to alternative sustainable routes to butenes, principally focussing on the dehydration of *n*-butanol to the corresponding butenes using zeolite catalysts, which offer high activity at lower reaction temperatures.[14] In this area, H-ZSM-5 has been a particular focus, in part as a result of the computational prediction of its high selectivity towards 1-butene by Reyniers and co-workers.[15] A number of laboratory studies have probed the kinetics of butanol dehydration using H-ZSM-5,[16] however these reactions were carried out at low butanol conversions and did not explore reaction selectivity. In contrast, Urresta [17] and Verberckmoes's group [18] have demonstrated that almost full conversion of *n*-butanol to a mixture of 1-, *cis*- and *trans*-2-butenes can be achieved at 260 °C after optimisation of the Si/Al ratio of the H-ZSM-5 catalyst employed.

Building on this established potential of H-ZSM-5 for *n*-butanol dehydration, H-ZSM-5 was the catalyst of choice for inclusion in our cascade flow process. Our experimental results confirmed that appropriately activated H-ZSM-5 did indeed perform well.[15] At 250 °C and with 0.024 mL min^{-1} flow rate, 98% conversion of butanol was achieved, with >99% butene selectivity being maintained for 4 hours on stream. Under these conditions a mixture of 1-butene (22%), *cis*-2-butene (29%) and *trans*-2-butene (49%) were obtained (Scheme 2). The only side product is di-*n*-butyl ether (DBE), with the extent of its formation being dependent on both reaction and reactor residence times, with slower space velocities resulting in a lower DBE make. The H-ZSM-5 catalyst maintains conversion of 95% for around 20 hours on stream (Figure 1) with <2% decrease in butene selectivity. However, after 70 hours, the conversion drops to ~58% (Figure S4), although DBE remains as the predominant side product (11% after 70 hours). Thus, based on this initial screening, H-ZSM-5 was deemed an appropriate *n*-butanol dehydration catalyst for use in the target cascade system.



Scheme 2. Conversion of *n*-butanol using H-ZSM-5 as catalyst. *Conditions: H-ZSM-5 (Si:Al 23, 0.1 g), catalyst pre-activated at 150 °C under N_2 flow for 1 h. Dehydration reaction carried out at 250 °C with 0.024 mL min^{-1} flow rate of n-butanol at atmospheric pressure; vaporiser and connections heat traced to 155 °C.*

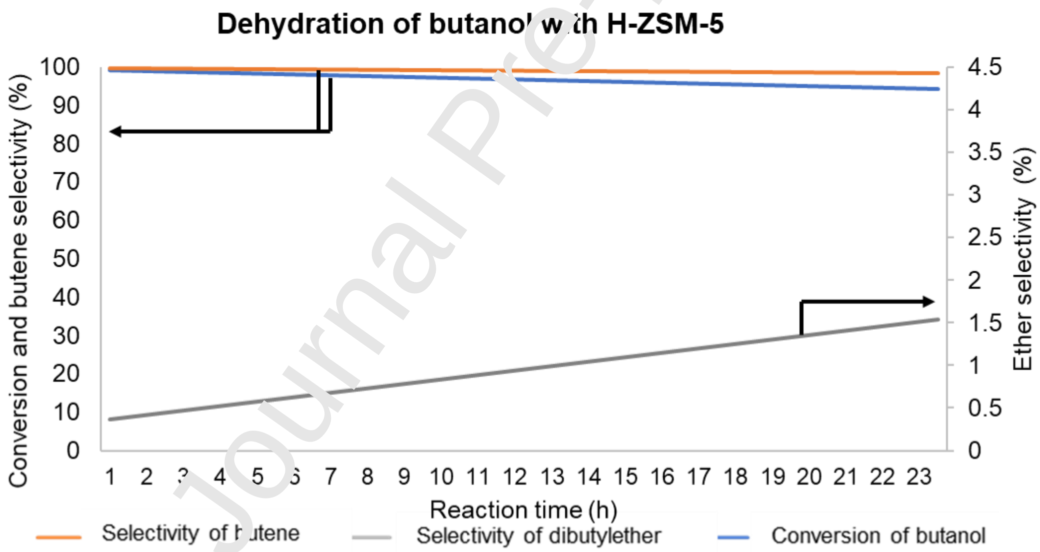


Figure 1. Conversion of *n*-butanol to butene with H-ZSM-5 at 250 °C, 0.024 mL min^{-1} flow rate for 24 hours on stream.

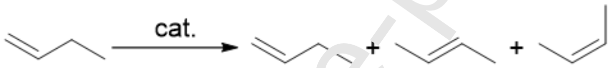
3.2. Isomerisation of 1-butene

Following selection of a suitable catalyst and operating parameters for *n*-butanol dehydration, focus moved to establishing reaction conditions for the necessary butene isomerisation step (Scheme 1, step B). Previously, it has been reported that isomerisation of 1- to 2-butene can be achieved using both homo- and hetero-geneous catalysts.[19] However, this project has focussed only on heterogeneously-catalysed routes. In this context, although 1-butene conversion of over 90% has been achieved using both a well-defined solid-state molecular organometallic (SMOM) catalyst and a MOF system with zeolite-type architecture at room temperature, these catalysts are either air-/moisture-sensitive or require high reaction pressures.[19][20] Consequently, this current study has instead explored the potential of a range of stable, cheap and robust commercially-available catalysts targeting high conversion at low reaction pressures. Based on prior literature, both silicon and magnesium oxides have shown good performance for the isomerisation of 1-butene and hence were selected as initial potential candidates in our study.[21] Additionally, computational studies by Marin's group have also suggested that zeolites are good potential candidates for butene isomerisation.[15] This is in agreement with our own observation that *trans*-2-butene was observed as the major product rather than 1-butene after *n*-butanol dehydration, suggesting that H-ZSM-5 is also active for the isomerisation of 1-butene. Consequently, H-ZSM-5 was also included in our catalyst screen.

Initial catalyst tests were performed using pure 1-butene as a model substrate and a gas flow rate of 6 mL min^{-1} to mimic the flow rate of the dehydration reaction (0.024 mL min^{-1} liquid flow rate). To ensure an accurate product composition analysis, reaction products from the flow reactor were collected using a gas sampling balloon, then dissolved in deuterobenzene, and analysed off-line by ^{1}H NMR spectroscopy.

The performance of appropriately activated silica, magnesium oxide, and zeolites were screened across a range of different reaction temperatures. With silica, only a 9% conversion is obtained at 300 °C, although on raising the reaction temperature to 400 °C the conversion increases to 72% with selectivities to *trans*-2-butene and *cis*-2-butene of 56% and 40%, respectively. Increasing the reaction temperature further to 500 °C does not improve conversion and results in formation of undesirable *iso*-butene (Table 1, Entry 1-4). Using MgO as catalyst even higher reaction temperatures are needed for isomerisation, with only 7% conversion being achieved at 400 °C with 63% and 37% selectivity to *trans* and *cis*-2-butene, respectively. Comparable conversion (~70%) to that obtained with silica at 400 °C is obtained at 500 °C, however, the on-set of isobutene (1%) formation is also observed (Table 1, Entry 5-7). Note, no isomerisation was observed in the absence of a catalyst.

Table 1. Screening results for 1-butene isomerisation with catalysts at different reaction temperatures.



Entry	Catalyst	T (°C)	Conv (%)	*trans*-2-butene (%)	*cis*-2-butene (%)	Isobutene (%)
1	SiO_2	20-250[a]	0	0	0	0
2	SiO_2	300	9	56	44	0
3	SiO_2	400	72	56	40	4
4	SiO_2	500	71	51	38	11
5	MgO	20-300[b]	0	0	0	0
6	MgO	400	7	63	37	0
7	MgO	500	70	57	43	1
8	H-Fer	20-50[c]	0	0	0	0
9	H-Fer	100	37	54	46	0
10	H-Fer	150	87	64	36	0
11	H-Fer	200	85	62	38	0
12	H-Fer	250	81	57	39	4
13	H-ZSM-5	20-50[c]	0	0	0	0
14	H-ZSM-5	100	25	56	44	0
15	H-ZSM-5	150	84	63	37	0
16	H-ZSM-5	200	85	62	38	0
17	H-ZSM-5	250	81	59	38	3
18	H-beta	20-50[c]	0	0	0	0
19	H-beta	100	20	50	50	0
20	H-beta	150	79	61	39	0
21	H-beta	200	83	62	37	1
22	H-beta	250	80	59	37	4

Conditions: catalyst (0.1 g) pressed and sieved to 250-500 microns, flow of 1-butene (6 mL min^{-1}), results analysed by ^{1}H NMR spectroscopy. [a]Individual reactions carried out at 20, 50, 100, 150, 200 and 250 °C, each gave no conversion. [b]Individual reactions carried out at 20, 50, 100, 150, 200, 250 and 300 °C, each gave no conversion. [c]Individual reactions carried out at 20 and 50 °C, each gave no conversion.

In contrast to silica and magnesium oxides, the zeolites H-ZSM-5, H-Beta and H-Fer all mediate 1-butene isomerisation at significantly lower operating temperatures (Table 1, Entry 8-22). For each of the zeolites, it was found that conversion increases upon raising reaction temperature, reaching a maximum at 150 °C. Operation at higher temperatures (up to 250 °C) results in the formation of small amounts of *iso*-butene (typically ~3%). Zeolite H-Fer gives the best results, 87% conversion, with selectivity to *cis*- and *trans*-2-butene of 36% and 64%, respectively, as the only products at 150 °C (Table 1, Entry 10). Increasing reactor residence time by doubling the H-Fer catalyst bed length has only a limited impact on conversion (89%), with selectivity essentially unchanged (*cis*- and *trans*-2-butene of 35% and 64%, respectively) at 150 °C, which suggests that a thermodynamic equilibrium has been reached under these operating conditions. Indeed, this observed equilibrium composition is in excellent agreement with that previously calculated, namely ~10% of 1-butene in the equilibrium mixture of 1-/2-butenes at 150 °C.[22] The results we have obtained here for the isomerisation of butenes using H-Fer as catalyst at atmospheric pressure are comparable to those for the isomerisation of butenes achieved using either a solid-state organometallic catalyst [19] or a MOF-based system at elevated pressure.[20] However, use of H-Fer is preferable since it is both easy to handle (air-/moisture stable) and operates at atmospheric pressure.

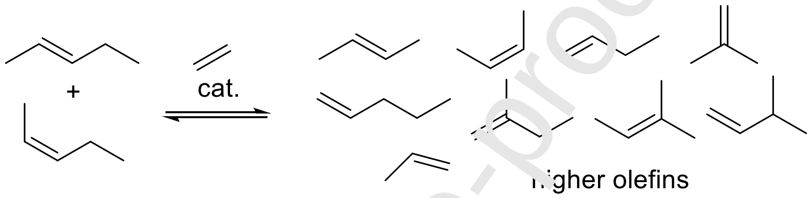
3.3. Cross-metathesis of *cis*-/*trans*-2-pentene with ethene

After the successful conversion of terminal butene to internal butenes, the next step in establishing a cascade for *n*-butanol to propene production was to establish a method for the conversion of the internal butenes to the target C_3 alkene *via* cross-metathesis with ethene (Scheme 1, step C). In the literature, silica- and/or alumina-supported molybdenum and tungsten catalysts have been reported to demonstrate appropriate olefin cross-metathesis performance with similar α-olefins.[23] However, the cross-metathesis performance of these classes of catalyst demonstrate significant substrate-specific reaction conditions. For example, propene/ethene cross metathesis can be achieved at 40 °C with MoO_3 on SiO_2/Al_2O_3,[24] while for pentene/ethene, over 500 °C is necessary to be obtain a reasonable conversion (~50 %) with either Mo or W supported on SBA-15 (a well-defined mesoporous silica).[25] Moreover, it is well established that the performance of olefin metathesis catalysts under industrially-relevant conditions is challenging as a result of low reaction rates and mediocre activities, which together necessitate forcing operating conditions. Consequently, for the current study, it was necessary to establish optimal reaction conditions for the specific substrates of interest, namely butenes.

Initially, determination of reaction conditions for the required ethene cross-metathesis transformation were explored using *cis*-/*trans*-2-pentene as substrate since this is an easily manipulable model liquid substrate, compared to gaseous butenes. Thus, cross-metathesis performance of a series of molybdenum- and tungsten-based catalysts supported on silica, silica-alumina and H-Y/alumina and SBA-15 supports were probed for conversion of ethene and *cis*-/*trans*-2-pentene (in a ratio 1:1, respectively) to butenes, measured over a period of one hour on stream (Table 2). Consistent with data from the literature for related heterogeneous metathesis catalysts,[25] no conversion of *cis*-/*trans*-2-pentene was obtained below 250 °C (Table 2). With the Mo on SiO_2/Al_2O_3 catalyst, the selectivity to butene was low even at 500 °C (Table 2, Entries 2 and 3), with the 2-pentenes principally being isomerised to 1-pentene and the three *iso*-pentenes. Changing the SiO_2/Al_2O_3 support to H-Y/Al_2O_3 made little difference (Table 2, Entry 4), while with silica as the support, the selectivity of butene increased to around 10% (Table 2, Entry 5). Encouragingly, however, with supported tungsten catalysts (W on SiO_2/Al_2O_3), 70% conversion of 2-pentenes was obtained with 49% selectivity to butenes, with the other products comprising 1-pentene, *iso*-pentenes and higher olefins (Table 2, Entry 6). Since it is known that acid washing of γ-Al_2O_3 leads to partial dissolution of alumina and results in a slight increase in the support's acidity and hence more active sites,[26] a similar process was tested with the SiO_2/Al_2O_3 support and any impact on subsequent cross-metathesis activity probed. Consequently, a series of new tungsten and molybdenum catalysts was prepared using nitric acid-washed SiO_2/Al_2O_3. The resulting molybdenum catalysts demonstrate a slight increase in butenes formation from 2% to 14% (Table 2, Entry 7 vs Entry 3) compared with that achieved employing the corresponding unmodified support. Significantly, the related tungsten/acid-washed SiO_2/Al_2O_3 supported catalysts show significantly better cross-metathesis activity, with 90% pentene conversion and 67% butene selectivity being obtained (Table 2, Entry 8, *c.f.* Entry 6, Figure 2). As observed for the catalysts with unmodified supports, operation at 500 °C is also essential for the systems with acid-washed SiO_2/Al_2O_3, with, for example, only 1% butene selectivity and 62% conversion to mainly isomerised products being obtained at 300 °C (Table 2, Entry 9). This performance enhancement achieved with the acid-washed supports is in good agreement with the notion that as a result of a Brønsted/Lewis acid synergy, dealuminated zeolite frameworks demonstrate significantly enhanced acidity, which is what is achieved here through acid washing.[27] Thus, we propose that for the W on acid-washed SiO_2/Al_2O_3 catalyst, the increased availability of Brønsted acid sites proximate to the assumed metathesis-active tungsten sites, namely the tungstacyclobutane intermediate (Chauvin mechanism), promotes their reactivity and hence cross-metathesis activity, as evidenced recently with zeolitic framework supports.[28]

Notably, this new, cheap, and readily accessible tungsten/acid-washed SiO_2/Al_2O_3-supported system shows better metathesis performance than the best previously reported heterogeneous cross-metathesis catalysts for ethene/pentenes. Under comparable operating conditions, tungsten/SBA-15 (Table 2, Entry 8 vs 10) performed less well (70% conversion, 32% butene selectivity) and required a higher reaction temperature of 550 °C (Table 2, Entry 11 vs Entry 8).[25] Thus, the tungsten on acid-washed SiO_2/Al_2O_3 catalyst was chosen for incorporation into the combined cascade system for ethene/butenes cross-metathesis where higher selectivity may be expected than with ethene/2-pentene since cracking rates increase dramatically with the carbon number of the olefinic substrate.[29]

Table 2. Screening of catalysts for 2-pentene/ethene cross-metathesis.



Entry	Catalyst	Temperature (°C)	Conversion (%)	Butenes selectivity (%)
1	Mo on SiO_2/Al_2O_3	400	0	0
2	Mo on SiO_2/Al_2O_3	250	65	0
3	Mo on SiO_2/Al_2O_3	500	60	2
4	Mo on H-Y/Al_2O_3	500	63	3
5	Mo on SiO_2 gel	500	64	11
6	W on SiO_2/Al_2O_3	500	70	49
7	Mo on acid-washed SiO_2/Al_2O_3	500	60	14
8	W on acid-washed SiO_2/Al_2O_3	500	90	67
9	W on acid-washed SiO_2/Al_2O_3	300	62	1
10	W on SBA-15	500	62	10
11	W on SBA-15	550	70	32

Reagents and conditions: catalyst (0.2 g) pressed, crushed, and sieved to 250-500 microns, flow of ethene (5 mL min^{-1}), flow of liquid 2-pentene (0.024 mL min^{-1}), results analysed by on-line GC-FID.

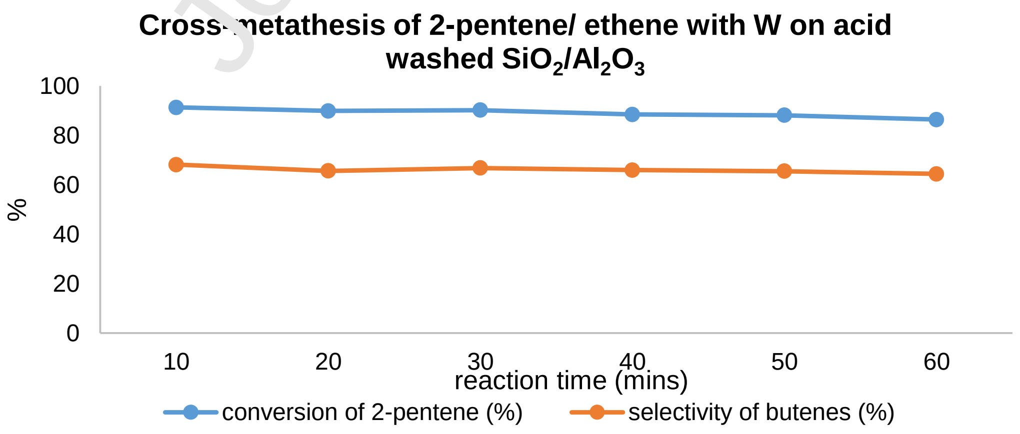


Figure 2. Conversion of 2-pentene to butenes with W on acid-washed SiO_2/Al_2O_3 500 °C, 0.024 mL min^{-1} flow rate for 2-pentene (Entry 8, Table 2).

3.4. Cascade catalysis system

With realistic catalysts and operating systems in hand, the next target was to couple the three reaction steps A-C, dehydration, isomerisation, and cross-metathesis (Scheme 1), into a single triple cascade flow sheet, Figure 3. To the best of our knowledge, only one previous report in the open literature has described this type of approach for the conversion of butanol to propene. Sieber and co-workers disclosed the use of a biocatalytic pathway employing Cytochrome P450 fatty acid decarboxylase OleT$_{JE}$ to convert sequentially butanol to butanal, butanal to butanoic acid and finally butanoic acid to propene in batch reactors.[30] In contrast, our method employing easily prepared heterogeneous catalysts in a flow system has the benefit of ease of catalyst/product separation as well as continuous operation.

To achieve a cascade process, a preliminary study employing a combination of three separately-heated reactor systems in series has been explored (Figure S4). *n*-Butanol was introduced into the system by a syringe pump with a flow rate of 0.024 mL min^{-1} and subsequently gasified in the vaporiser (155 °C) before passing sequentially into reactors 1 and 2, with the resultant product stream then being mixed with ethene (flow rate of 6 mL min^{-1}) prior to entry into reactor 3 (estimated ratio of butenes:ethene ~1:1). The final product gas stream was analysed on-line using a GC-FID. An overall *n*-butanol to propene yield of 64% was obtained using W on acid-washed SiO_2/Al_2O_3. This level of unoptimized *n*-BuOH to propene conversion in a single flow sheet is particularly noteworthy since the best performing heterogeneous catalyst for just the step involving cross-metathesis of pure ethene/*trans*-2-butene, namely zeolite USY-supported WO_x, achieves a propene yield of 79% with 80% selectivity.[31] Indeed, other established cross-metathesis catalysts for the conversion of butenes to propene, such as W-H/Al_2O_3,[32] and mixed $WO_3/SiO_2/MgO$,[33] both demonstrate comparable performance to that of the best WO_x-containing commercial catalyst.[33]

We suggest that the moderate overall conversion and selectivity achieved herein by linking catalytic systems comprising H-ZSM-5, H-Fer, and W on acid-washed SiO_2/Al_2O_3 in series is a result of several factors. The water produced from the initial *n*-butanol dehydration reaction is likely to interact detrimentally with the Lewis acidic tungsten centre of the cross-metathesis catalyst. Additionally, both the dehydration and isomerisation steps result in a mixture of isomeric butenes, not least a mixture of *cis*-/*trans*-2-butene, which is problematic since the rate of cross-metathesis of *cis*-2-butene is considerably slower than that of *trans*-2-butene.[34] It is also well established that water can cause irreversible zeolite deactivation due to dealumination.[35] It is likely that an improved process will need to incorporate a water removal step.

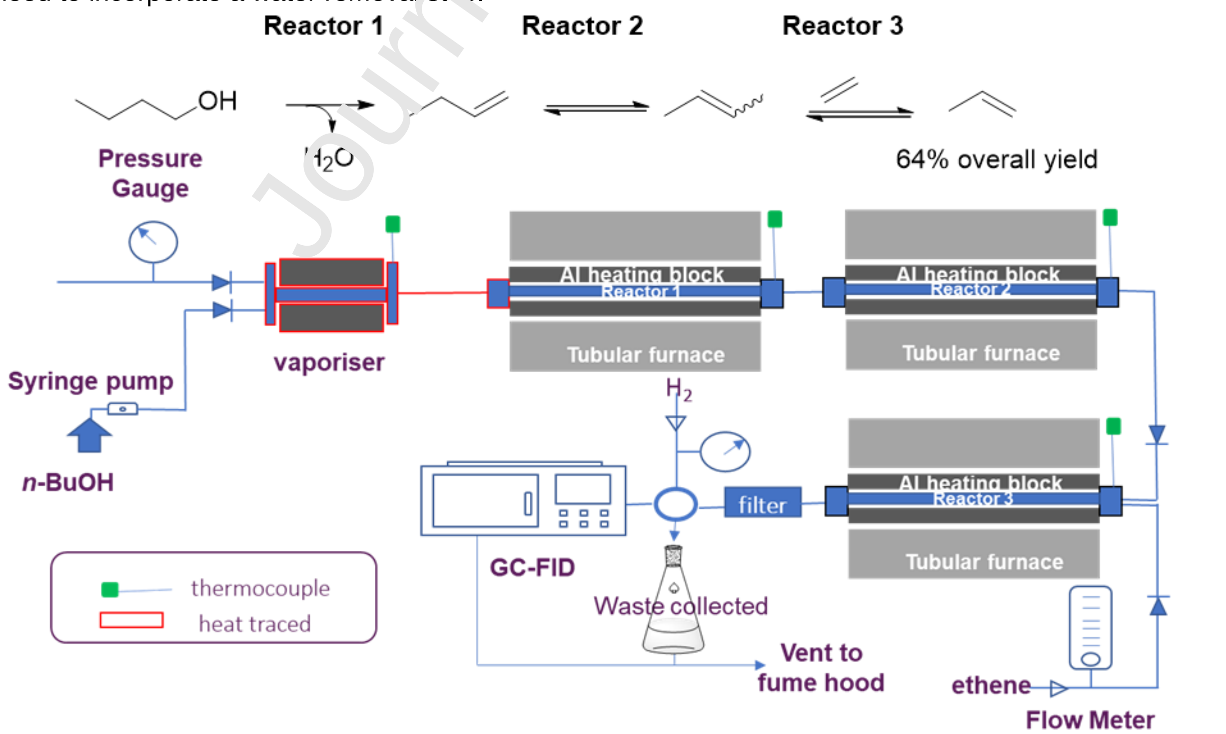


Figure 3. Overall reaction scheme and reactor arrangement used to convert *n*-BuOH to propene in a triple cascade.

4. Conclusion

A catalyst screening study has shown that the appropriately treated zeolites H-ZSM-5 and H-Fer show good activities, conversions, and lifetimes for *n*-butanol dehydration and butene isomerisation, respectively. Similarly, the work presented herein shows that a novel, cheap, and readily prepared, but unoptimised tungsten on acid-washed SiO_2/Al_2O_3 catalyst gives encouraging butene/ethene cross-metathesis performance. Building on information derived from these three independent screening/evaluation studies, we have demonstrated the possibility of using a simple three-reactor cascade process for the conversion of *n*-butanol to propene in flow. Although only moderate conversions and selectivities have been achieved, it is anticipated that further optimisation, principally incorporating water removal stages, will lead to a viable catalytic methodology for the commercial production of the key feedstock propene from a bio-derived *n*-butanol feed and that developing systems realistic catalyst lifetimes is likely to be challenging.

Author contributions

Y.S., A.J.B., A.S.W., and P.W.D. contributed to the design of the study; Y.S. conducted experiments and data analysis. Y.S wrote the manuscript and supporting information, with all authors commenting on and amending both documents. All authors discussed and contributed to the work.

Conflicts of interest

There are no conflicts of interest to declare.

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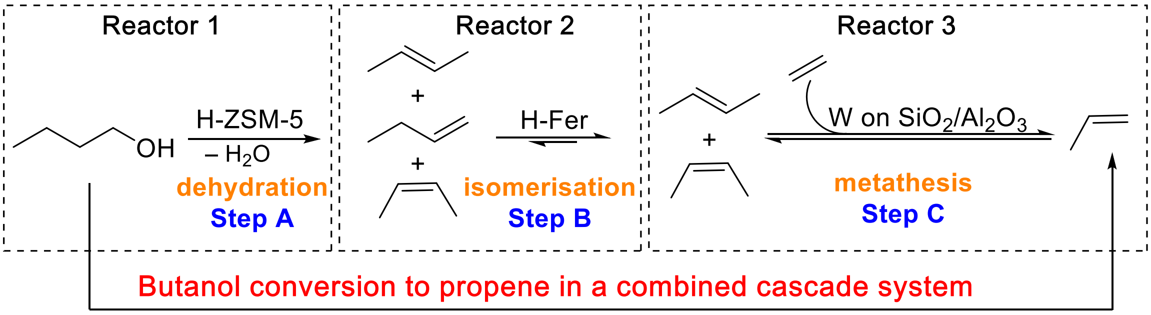
Credit Author Statement

Y.S., A.J.B., A.S.W., and P.W.D. contributed to the design of the study; Y.S. conducted experiments and data analysis. Y.S wrote the manuscript and supporting information, with all authors commenting on and amending both documents. All authors discussed and contributed to the work.

Conflicts of interest

There are no conflicts of interest to declare.


Reactor 1
Reactor 2
Reactor 3
OH
H-ZSM-5
– H2O
dehydration
Step A
+
+
H-Fer
isomerisation
Step B
+
W on SiO2/Al2O3
metathesis
Step C
Butanol conversion to propene in a combined cascade system

- H-ZSM-5 dehydrates *n*-butanol to *n*-butenes with 98% conversion and >99% selectivity.
- Isomerisation of 1-butene to 2-butenes over H-Fer gives equilibrium composition.
- W on acid-washed silica/alumina is a promising olefin cross-metathesis catalyst.
- *n*-Butanol is converted to propene in 64% yield using a triple cascade flow system.