The continuous self aldol condensation of propionaldehyde in supercritical carbon dioxide: a highly selective catalytic route to 2-methylpentenal†

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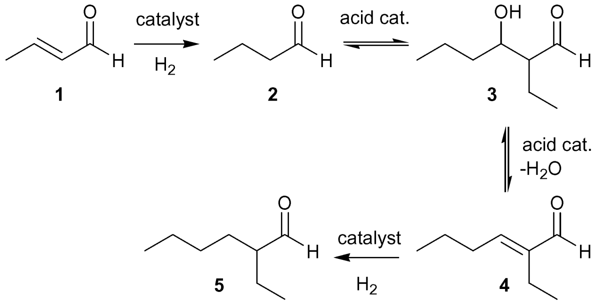
The aldol reactions of propionaldehyde and butyraldehyde have been explored in supercritical CO_2, $scCO_2$, using an automated continuous flow reactor. The reaction was found to proceed over a variety of heterogeneous acidic and basic catalysts and with increased selectivity compared to using neat reactants.

Introduction

The aldol reaction is one of the most widely used reactions for C–C bond formation,[1,2] yet it has several drawbacks from an environmental standpoint. Some of these issues have been highlighted by Mestres[3] and Kelly *et al*.[4] Industrially, the aldol synthesis has to overcome poor selectivity[3] and the use of stoichiometric quantities of aqueous base with neutralisation and separation of the aldol product after completion of the reaction. This neutralisation generates large volumes of aqueous inorganic waste which require disposal.[4]

The continuous synthesis of 2-ethylhexanal (**5**), a commercially important aldol product, from crotonaldehyde (**1**) has been elegantly demonstrated by Baiker and co-workers,[5,6] who performed the reaction continuously in $scCO_2$ over a palladium doped acidic resin (Amberlyst® 15) Scheme 1. Their process combined the aldol condensation and the hydrogenation of the unsaturated aldol product into a single process, hence driving the reaction equilibrium. They achieved >99% hydrogenation of **1** to **2** but the further conversion to **5** (*via* the hydrogenation of the aldol intermediate, **4**) only reached a maximum of 70%. However, they were unable to produce **5** directly from **2** with high selectivity.



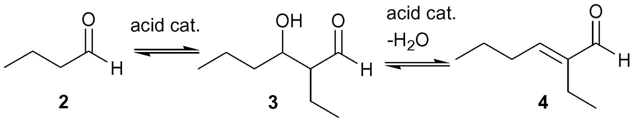
Scheme 1 The hydrogenation[5,6] of crotonaldehyde (**1**) to yield butyraldehyde (**2**), with subsequent self aldol condensation to form 2-ethylhexenal (**4**) and hydrogenation of the unsaturated aldol product to form 2-ethylhexanal (**5**).

The work described in this paper aims to build on the work carried out by Baiker and co-workers by studying the aldol reaction further in $scCO_2$, and by exploring whether the use of hydrogen can be avoided and, hence, whether unsaturated aldols can be produced with high selectivity. Hydrogen acts as a driving force in Scheme 1 because **5** does not participate in the acid catalysed equilibrium steps, thus forcing the reaction towards the saturated aldehyde product.

All our reactions were carried out on an automated continuous reactor[7] which is described briefly in the Experimental section at the end of the paper. The reactor has on-line GC analysis. This allows the operator to program a series of reaction conditions, for example ramping of the temperature, while analytical data are collected automatically under computer control.

Proof of concept

The self aldol reaction of butyraldehyde (**2**) was explored over Amberlyst® 15 in continuous flow *without* the addition of hydrogen (Scheme 2) utilising $scCO_2$ as the reaction medium. This is the first stage of the reaction that Baiker and co-workers reported to give only 70% of the saturated aldehyde **5**. Fig. 1 shows the conversion of **2** and selectivity to **4** as a function of reactor temperature at 8 MPa pressure with fixed flow rates of both CO_2 and **2**. It can be seen that the conversion increases over the whole temperature range studied. A marked increase in the selectivity is also observed from 50 to 70 °C, but above this temperature the selectivity for **4** remains constant and high, >90%.



Scheme 2 Self aldol condensation of **2** showing both the aldol intermediate (**3**), and the unsaturated dehydration product (**4**).

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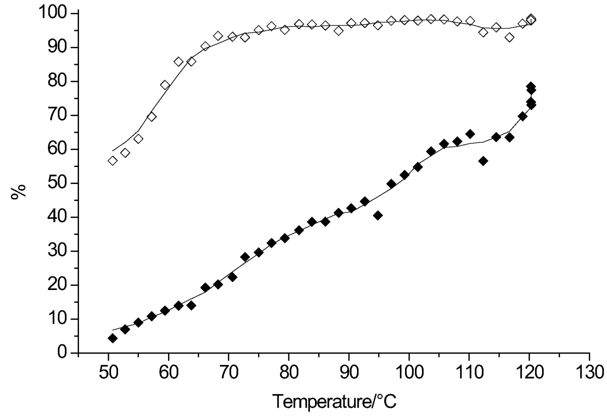
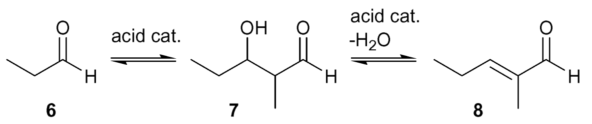


Fig. 1 The formation of the unsaturated butyraldehyde aldol product **4** in $scCO_2$ showing the temperature dependence of the conversion (◆) and selectivity (◇) of the self aldol condensation of **2** at flow rates of 0.1 mL min^{-1} of **2** and 1.0 mL min^{-1} of CO_2 at 8 MPa using a 10 mL reactor filled with Amberlyst® 15.

This result indicates that it is indeed possible to conduct the aldol reaction effectively in $scCO_2$ using a heterogeneous acid catalyst to produce the unsaturated aldol product in high yields.

Reaction of propionaldehyde

Following this successful proof of concept experiment with butyraldehyde, we have studied the self aldol condensation of propionaldehyde (**6**) to yield 2-methylpentenal (**8**) (Scheme 3).



Scheme 3 The self aldol condensation of propionaldehyde (**6**) showing both the aldol intermediate, 3-hydroxy-2-methylpentanal (**7**), and the unsaturated dehydration product 2-methylpentenal (**8**).

Aims and strategy

Compound **8** is a commercially important compound that is used widely in the fragrance, flavour,[8] and cosmetic industries[9] as well as being an important intermediate in the synthesis of pharmaceuticals[10,11] and plasticisers.[12] Compound **8** is manufactured industrially by the aldol condensation of **6** in the presence of stoichiometric amounts of an aqueous base such as NaOH or KOH. Under optimum conditions, 99% conversion of **6** is achieved with 86% selectivity to **8**. Additionally, it has been demonstrated that the inclusion of an inert solvent can reduce the formation of any unwanted by-products.[12]

Mehnert *et al.* have studied the base catalysed aldol condensation of **6** in ionic liquids. They reported 100% conversion at 80 °C in 3 h with 83% selectivity for **8** using NaOH in $[BMIM][PF_6]$.[13,14] The solvent-free condensation of **6** has also been explored using a batch process at 100 °C using solid base catalysts by Sharma *et al.*[15] Their optimum results were achieved using an activated Mg/Al hydrotalcite catalyst, giving 97% conversion of the **6** with 99% selectivity to **8**. The aldol condensation of **6** has also been carried out by Scheidt[16] in the gas phase over lithium phosphate at 270 °C. This gave 95% selectivity to **8** at 32% conversion of **6**.

Table 1 Maximum yield of **8** achieved during temperature ramp over various catalysts from the self condensation of **6** at flow rates of 0.1 mL min^{-1} **6**, 1.0 mL min^{-1} CO_2 at 10 MPa (*base catalysts in italics*)

Catalyst	% Yield **8**[a]	% Sel. **8**	Temp/°C
γ-Alumina	78	89	210
Amberlyst® 15	76	88	135
Amberlyst® A26	*10*	*83*	*180*[b]
Deloxan® ASP	49	77	125
Magnesium oxide	*39*	*95*	*240*
Nafion® SAC13	48	84	125
Purolite® CT175	63	81	155
Supported NaOH	*70*	*83*	*285*

[a] Determined by GC. [b] Catalyst undergoing rapid degradation.

Matsui *et al.*[17,18] have explored the effect of a pressure of CO_2, in a batch reaction, on the selectivity of the aldol condensation of **6** whilst using a MgO catalyst. At 12 MPa, under supercritical conditions, 94% selectivity towards **8** was achieved, whereas at the subcritical pressure of 5 MPa, 85% selectivity towards the aldol product was observed.

Our aim was to use the continuous flow $scCO_2$ apparatus[7] to screen rapidly a variety of both acidic and basic heterogeneous catalysts, see Table 1, for their suitability for the selective self condensation of propionaldehyde across a range of temperatures. Once a suitable catalyst has been found it would then be tested under a wide variety of conditions to optimise the performance of the reaction further. The high solubility of gaseous hydrogen and organic compounds in $scCO_2$[19] can be used in combination with the aldol reaction to allow hydrogenation of the unsaturated product *in situ* if desired.[5,6]

Catalyst screening

For each catalyst system the reaction was performed using identical reaction conditions at a pressure of 10 MPa. Further details of the catalysts used in this study are outlined later in Table 4 (Experimental section). Fig. 2 shows the conversion and selectivity towards **8** for each catalyst across the temperature range tested. The maximum yields are summarised in Table 1. However, from the point of view of environmental sustainability, selectivity towards the desired product, Table 2, is more important than conversion, because of the ease of separation of unreacted **6** from the product **8** by simple distillation due to the large difference in boiling point of the two compounds; this enables unreacted **6** to be easily repassed through the reaction system.

At temperatures <70 °C, with Brønsted acid catalysts such as Amberlyst® 15 or Purolite® CT-175 (Fig. 2b and 2e), the by-products consisted of the aldol intermediate, **7**, and a variety of other compounds including C_9 aldehydes. These arise from further aldol reactions, and Michael additions to the α,β-unsaturated product **8**. A typical product distribution can be seen in the gas chromatogram, shown in Fig. 3.

A similar profile of conversion and selectivity was obtained with the basic catalyst, NaOH/silica, although higher temperatures were required to achieve this reactivity (Fig. 2h). Magnesium oxide (Fig. 2f) also gave excellent selectivity albeit with a poor conversion. The experiments suggested that the MgO underwent rapid deactivation with a decrease in the

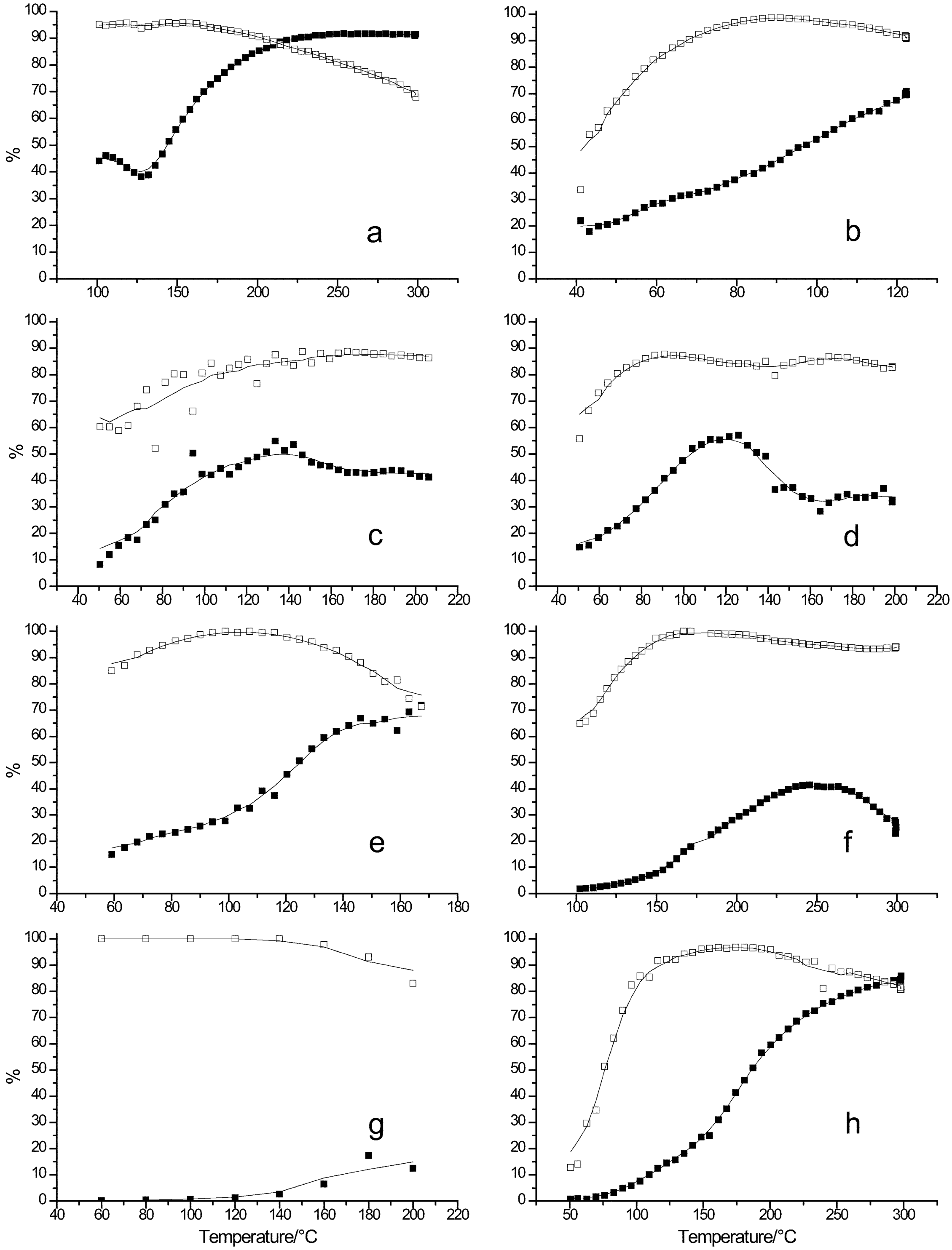


Fig. 2 Summary of catalyst performance over a range of temperatures, showing rare examples of base catalysis in $scCO_2$. The plots show the temperature dependence of the conversion (■) and selectivity (☐) of the self aldol condensation of **6** to **8** in the presence of a variety of catalysts, each packed into a 10 mL reactor tube. The reactions were carried out at flow rates of 0.1 mL min^{-1} of **6** and 1.0 mL min^{-1} of CO_2 at 10 MPa. The catalysts are: **Amphoteric**: a, γ-alumina; **Brønsted acids**: b, Amberlyst® 15; c, Deloxan® ASP IV/6–2; d, Nafion® SAC-13; e, Purolite® CT-175; **Bases**: f, magnesium oxide; g, Amberlyst® A26; h, supported NaOH. A moving average line has been drawn between data points to aid visualisation.

conversion as the temperature was increased over time. This rapid deactivation may be due to the removal of catalytically active hydroxide groups from the surface of MgO. The freshly exposed MgO can then form inactive carbonates upon reaction with CO_2.[20] Amberlyst® A26 had poor activity (Fig. 2g) with only minor conversion over the temperature range studied. This is probably due to the formation of carbamate species by the reaction of CO_2 with the amine groups of the catalyst.

Table 2 Maximum selectivity achieved during temperature ramp over various catalysts for the self condensation of **6** at flow rates of 0.1 mL min^{-1} **6**, 1.0 mL min^{-1} CO_2 at 10 MPa (*base catalysts in italics*)

Catalyst	% Conv. **6**[a]	% Sel. **8**	Temp/°C
γ-Alumina	46	96	158
Amberlyst® 15	43	99	95
Amberlyst® A26	*7*	*97*	*160*[b]
Deloxan® ASP	50	89	146
Magnesium oxide	*22*	*>99*	*184*
Nafion® SAC13	47	87	100
Purolite® CT175	37	>99	116
Supported NaOH	*41*	*97*	*174*

[a] Determined by GC. [b] Catalyst undergoing rapid degradation.

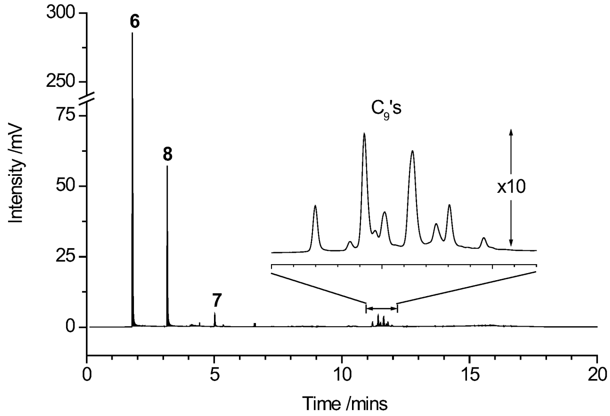


Fig. 3 GC chromatogram (see Experimental for details) taken from Fig. 2b. This shows the range of products from the self condensation of **6** over Amberlyst® 15 at 50 °C. The main peaks are due to **6**, **7** and **8**; the inset figure shows the region from 11.0–12.2 mins with expanded scales. (Other minor peaks remain unidentified.)

Lower selectivity was achieved with Nafion® SAC13 than with Amberlyst® 15 possibly because the higher acidity of Nafion® accelerated the rate of side reactions. Proportionately more **7** was formed at <60 °C with up to 10% selectivity. Even at 140 °C there was up to 5% selectivity towards **7** with Nafion® SAC13.

Overall, γ-alumina, Amberlyst® 15, and Purolite® CT-175 appeared to have the greatest potential for further optimisation whilst maintaining a high selectivity for **8**.

Optimisation of the reaction with Amberlyst® 15

Following the catalyst screening, Amberlyst® 15 was chosen for optimisation due to its low operating temperature, high selectivity and high yield compared to Purolite® and γ-alumina (Table 1). Optimisation of the reaction in $scCO_2$ was carried out by varying several reactor parameters. Firstly, the reaction was carried out under the same conditions both with and without CO_2. Three reactions were performed to study the effect of CO_2 on the system: 0.1 mL min^{-1} **6** without CO_2; 0.5 mL min^{-1} **6** without CO_2; 0.1 mL min^{-1} **6** with 1.0 mL min^{-1} CO_2, these results are shown in Fig. 4, Fig. 5 and Fig. 6. The $scCO_2$ reaction system produced much lower amounts of **7**, the aldol intermediate, to **8**.

Similarly, Fig. 5 shows that the presence of $scCO_2$ increases the selectivity toward the desired product **8**. However, the conversion at low temperatures was significantly higher *without* CO_2 (Fig. 6). As the temperature was increased, the conversion in $scCO_2$ increased markedly and $scCO_2$ has little effect on conversion at ≥130 °C.

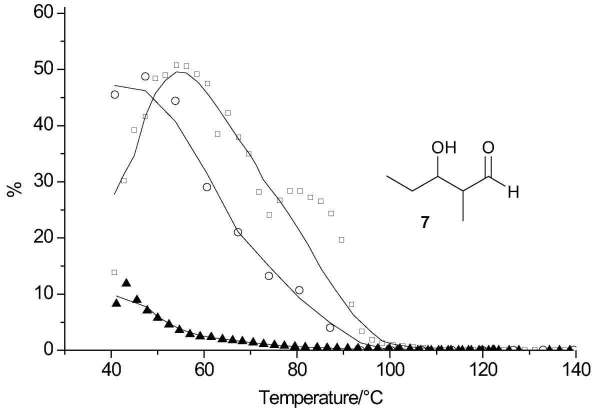


Fig. 4 Demonstration of how the addition of CO_2 reduces the amount of the intermediate **7** in the product stream at lower temperatures. The plot shows the temperature dependence of the selectivity for **7** during the self aldol condensation of **6** over Amberlyst® 15 at 10 MPa, flow rates of: □, 0.1 mL min^{-1} of **6**, no CO_2; ○, 0.5 mL min^{-1} of **6**, no CO_2; ▲, 0.1 mL min^{-1} of **6** and 1.0 mL min^{-1} of CO_2.

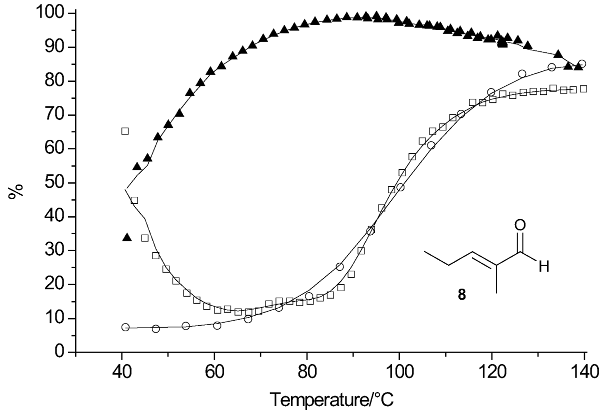


Fig. 5 Plot demonstrating the increase in selectivity for **8** in the presence of CO_2 during the self aldol condensation of **6** over Amberlyst® 15. Carried out at 10 MPa, flow rates of: □, 0.1 mL min^{-1} of **6**, no CO_2; ○, 0.5 mL min^{-1} of **6**, no CO_2; ▲, 0.1 mL min^{-1} of **6** and 1.0 mL min^{-1} of CO_2.

It is postulated that the reaction is driven to completion by the insolubility of the polar aldol intermediate **7** in $scCO_2$. Intermediate **7** will most likely exist in a liquid-like phase with a higher affinity for the catalyst surface. It can then react forming **8** which is then removed from the catalyst due to its higher solubilty in $scCO_2$. See ESI† for details of phase behaviour of **6** and **8** in $scCO_2$ – unfortunately it was not possible to isolate the intermediate **7** in sufficient purity to analyse its phase behaviour with CO_2.

Because the selectivity is higher for the reaction in $scCO_2$, the overall yield of **8** is higher with CO_2, than without, between 60 and 140 °C (see Fig. 6).

Entries 1–4 in Table 3 show the effect of altering the residence time by varying the flow rates of CO_2 and **6** whilst maintaining a constant 6 mol% organic ratio at an isothermal reactor temperature of 90 °C. As the residence time was decreased, a

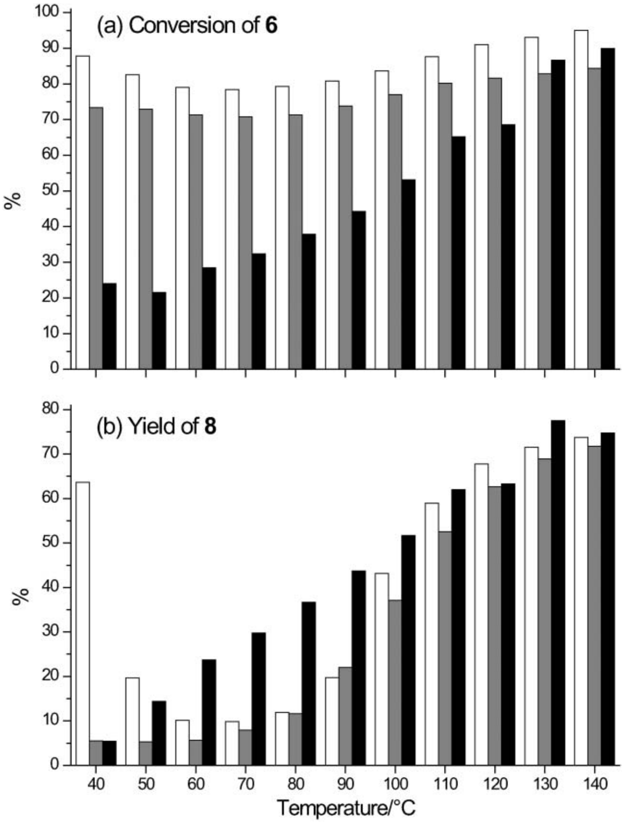


Fig. 6 At lower temperatures the conversion of **6** is higher without CO_2, but the yield of **8** is higher with CO_2 due to the significant increase in selectivity. Temperature dependence of: (a), the conversion of **6** during its self aldol condensation over Amberlyst® 15 and (b), the yield of **8** from the self condensation of **6** over Amberlyst® 15 is illustrated. Carried out at 10 MPa, flow rates of: □, 0.1 mL min^{-1} of **6**, no CO_2; ▨, 0.5 mL min^{-1} of **6**, no CO_2; ■, 0.1 mL min^{-1} of **6** and 1.0 mL min^{-1} of CO_2.

marginal decrease in conversion was observed (51% → 44%, as total flow rate was increased from 0.825 mL min^{-1} → 3.85 mL min^{-1}). To test further the effect of residence time a second reactor was added downstream of the first. Fig. 7 shows that an additional catalyst bed gives an extra 20% in conversion from 60 to 105 °C, accompanied by an increase in selectivity to >99%.

Entries 5–8 in Table 3 show that the molar ratio of CO_2 : **6** has only a minimal effect on the conversion and selectivity of the reaction. Therefore, the benefits of using CO_2 on selectivity can be retained even when using high concentrations of **6**.

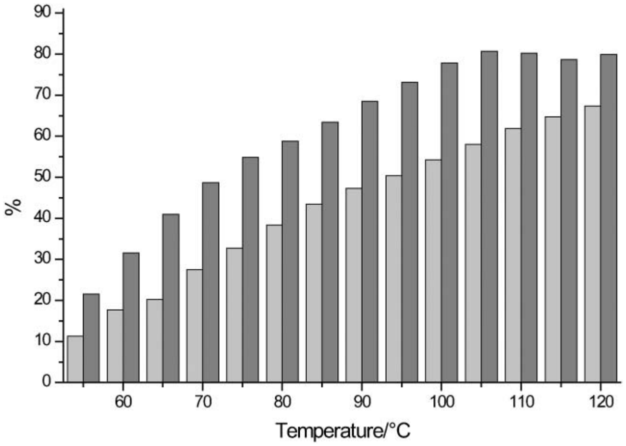


Fig. 7 Effect of temperature on the yield of **8** with: ▤, a single reactor; ▨, two reactors in series (doubling the reactor volume). Carried out at flow rates of 0.1 mL min^{-1} of **6** and 1.0 mL min^{-1} of CO_2 at 8 MPa in the presence of Amberlyst® 15. The addition of a second reactor had no observable effect on the selectivity.

The effect of pressure was also explored (Table 3, $N = 9$–12). No definitive change in selectivity was observed as the pressure was varied from 6 to 20 MPa.

The activity of the catalyst was monitored over time under constant conditions of 90 °C and 8 MPa with no pre-equilibration of the system. These conditions were chosen to maximise the conversion with >99% selectivity. There was a rapid reduction in conversion from 86% to 50% over the first 8 h with a small percentage of side products being observed. The conversion then stabilised at 43% and was maintained at this level up to 65 h with no observable side products (by GC) (Fig. 8). A loss of activity was also observed by Baiker and co-workers[5] when performing the aldol reaction in $scCO_2$. The stabilisation of conversion following an initial rapid drop suggests that a partial desulfonation of Amberlyst® 15 has occurred, rather than a coking process. We have previously observed a similar desulfonation with the Friedel–Crafts alkylation of anisole.[21]

The *in situ* hydrogenation of the unsaturated product **8** is also of interest, see Scheme 4. The hydrogenation was carried out by replacing the Amberlyst® 15 with a 50 wt% mixture of

Table 3 Study on the effect of reaction parameters on the conversion and selectivity of **6** to **8**

N	T/°C	P/MPa	CO_2 flow/mL min^{-1}	**6** flow/mL min^{-1}	Mol% of **6**	Conv. (%)	Sel. (%)
1[a]	90	10	**0.75**	**0.075**	6	51	95
2[a]	90	10	**1.00**	**0.100**	6	48	92
3[a]	90	10	**2.25**	**0.225**	6	46	96
4[a]	90	10	**3.50**	**0.350**	6	44	95
5[b]	120	10	0.97	1.027	**40**	56	90
6[b]	120	10	1.04	0.645	**28**	57	88
7[b]	120	10	1.10	0.335	**16**	50	88
8[b]	120	10	1.15	0.077	**4**	59	87
9[c]	120	**6**	1.00	0.100	6	66	64
10[c]	120	**10**	1.00	0.100	6	71	65
11[c]	120	**15**	1.00	0.100	6	62	68
12[c]	120	**20**	1.00	0.100	6	68	76

The parameters were varied as follows: [a] residence time; [b] concentration of substrate **6**; [c] system pressure.

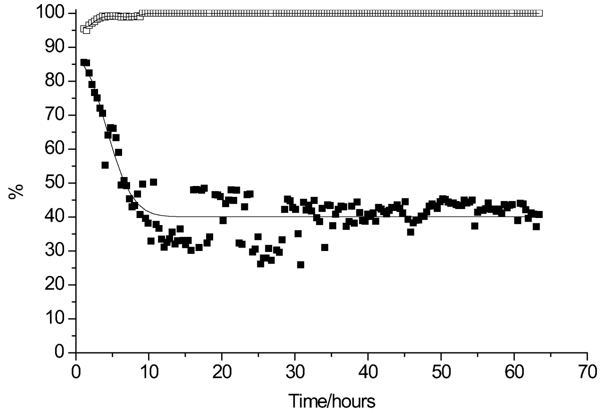
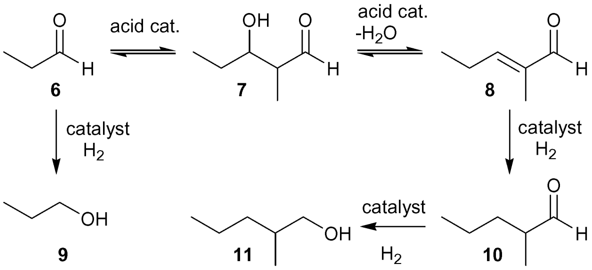


Fig. 8 Effect of catalyst activity over an extended time period on the conversion (■) and selectivity (□) of the self aldol condensation of **6** to **8** in the presence of Amberlyst® 15. The catalyst was loaded into two reactors in series and the reaction was carried out isothermally at 90 °C, 8 MPa with flow rates of 0.1 mL min^{-1} of **6** and 1.0 mL min^{-1} of CO_2.



Scheme 4 Self aldol condensation of propionaldehyde (**6**) with possible hydrogenation products: propan-1-ol (**9**), 2-methylvaleraldehyde (**10**) and 2-methyl-1-pentanol (**11**).

Amberlyst® 15 and 2% Pd on silica/alumina (Johnson Matthey Type 31) and dosing hydrogen into the system at 0.55 molar equivalents (based on **6**). Fig. 9 shows the conversion of **6** and selectivity to **10** as a function of temperature. No hydrogenation of the carbonyl group to **11** was observed even when complete hydrogenation of **8** was achieved. The conversion was slightly elevated higher than that achieved with Amberlyst® 15 alone (Fig. 7) suggesting that the hydrogenation of **8** to **10** may drive the dehydration of **7** to some extent.

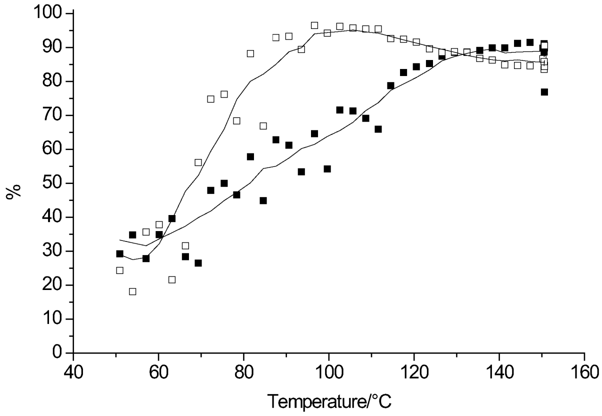


Fig. 9 Plot of the temperature dependence of the conversion (■) and selectivity (□) of the self aldol condensation and *in situ* hydrogenation of **6** to **10** in the presence of Amberlyst® 15 mixed with 2% Pd on silica/alumina (JM Type 31). The reactions were carried out at flow rates of 0.1 mL min^{-1} of **6** and 1.0 mL min^{-1} of CO_2 at 8 MPa with 0.55 equivalents of hydrogen. No hydrogenation of the carbonyl group to **9** or **11** was observed.

Conclusions

The self condensation of butyraldehyde and propionaldehyde in $scCO_2$ has been successfully conducted, yielding the α,β-unsaturated aldol products with high selectivity. A series of catalysts has been evaluated, using an automated continuous flow reactor. Surprisingly, two basic catalysts were effective in $scCO_2$, but overall the experiments showed that Amberlyst® 15 was the most effective of the catalysts screened. The reaction parameters with Amberlyst® 15 parameters were then studied in more detail. The formation of the unsaturated aldol product, **8**, was more selective in $scCO_2$ than in neat propionaldehyde, over the whole temperature range studied, an effect attributed to the postulated insolubility of the polar aldol intermediate, **7**, in $scCO_2$. The additional selectivity which is observed in the $scCO_2$ system delivers higher yields of **8**, whilst any unreacted starting material could be easily recycled. Finally, it was possible to perform an *in situ* hydrogenation of **8** by using a mixed catalyst bed consisting of a 50 wt% mixture of Amberlyst® 15 and 2% Pd on silica/alumina (Johnson Matthey Type 31) producing 2-methylvaleraldehyde in high yield. Thus, overall, our experiments demonstrate that aldol condensations in $scCO_2$ have even wider potential than reported by previous workers in this field.

Experimental

Safety hazard

CAUTION! *The experiments described in this paper involve the use of relatively high pressures and require equipment with the appropriate pressure rating.*

Catalysts and reagents

Commercially available catalysts were employed: γ-alumina (SI Group), Amberlyst® 15 (Lancaster Synthesis), Amberlyst® A26 (Alfa Aesar), Deloxan® ASP (Degussa Hüls), magnesium oxide (Acros), Nafion® SAC 13 (Sigma Aldrich), Purolite® CT-175 (Purolite International Ltd). NaOH was used as NaOH on a silica support, see Table 4. Commercially available propionaldehyde (Acros, 97%) and butyraldehyde (Acros, 97%) were used without further purification.

Automated continuous flow apparatus and reaction procedure

Fig. 10 shows a schematic view of the experimental apparatus. A programmable CO_2 pump, CP (Jasco PU-1580-CO_2) and HPLC pump, OP (Jasco PU-980) were connected to a 1/4 inch tee-piece, packed with glass beads, PH. The tee-piece acts as both mixer and pre-heater, heated by cartridge heaters within an aluminium heating block. Hydrogen was dosed into the system *via* a 6-port Rheodyne, HD, and was premixed with the CO_2 in a static mixer, M. The reactor, R, consisted of a 10 mL 316 SS tube (100 mm × 12 mm OD), packed with catalyst and heated by cartridge heaters

Table 4 Catalysts employed in this study

Catalyst	Support	Active group	Catalyst loading
γ-Alumina	N/A	N/A[a]	N/A
Amberlyst® 15	Macroreticular polystyrene cross-linked with divinylbenzene	$-SO_3H$	4.7 eq/kg
Amberlyst® A26	Macroreticular polystyrene cross-linked with divinylbenzene	$-N(Me)_3OH$	0.80 eq/L
Deloxan® ASP IV/6–2	Polysiloxane	$-SO_3H$	Unknown
Magnesium oxide	N/A	N/A[a]	N/A
Nafion® SAC13	Copolymer resin (of tetrafluoroethane and perfluoro-2-(flurosulfonylethoxy)propyl vinyl ether)	$-CF_2CF_2SO_3H$	0.13 eq/kg
Purolite® CT-175	Macroporous polystyrene cross-linked with divinylbenzene	$-SO_3H$	4.9 eq/kg
Supported NaOH	Silica	NaOH	3.5 eq/kg

[a] The metal oxides, Al_2O_3[22] and MgO[20] possess a variety of different active sites and modes of catalysis.

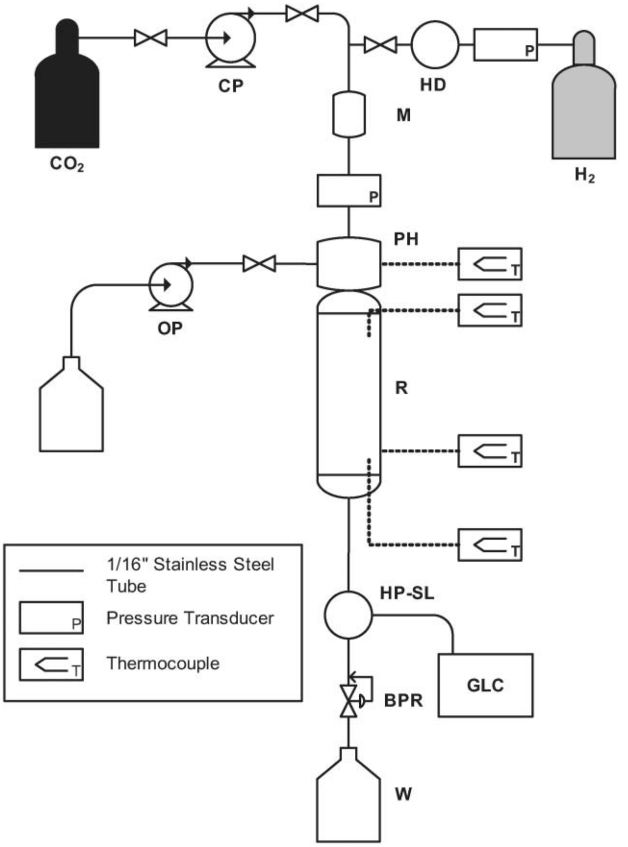


Fig. 10 Schematic of the automated supercritical fluid continuous flow apparatus. The components are labelled as follows: **CP**, chilled CO_2 pump; **HD**, H_2 dosing unit; **M**, mixer; **OP**, organic pump; **PH**, pre-heater and mixer; **R**, reactor; **HP-SL**, high pressure sample loop; **BPR**, back pressure regulator; **GLC**, gas liquid chromatograph; **W**, organic waste.

in an aluminium heating block, controlled *via* a programmable heating controller (Eurotherm 2416). The mixture of products and gases passed through a HPLC 4-port sample loop, HP-SL, which injects the sample into the carrier gas flow of a GLC (Shimadzu GC-17A), where product separation and analysis was carried out.

The system pressure was maintained by a programmable Back Pressure Regulator, BPR (Jasco BP-1580-81). Products were collected in the waste bottle, W. The temperature and pressure was logged at several points throughout the system on a computer, *via* a PicoLog® data recorder.

In a typical experiment, the reactor was filled with catalyst and sealed into the apparatus. After the equipment had stabilised at the required pressure and flow rate of CO_2, the reactor was heated to the reaction temperature and the substrate was pumped into the system. Experimental parameters were programmed into the pumps, back pressure regulator and GC. Unless otherwise stated, the standard reaction conditions were: flow of CO_2 1.0 mL min^{-1} at −10 °C and 5.8 MPa, flow of the substrate 0.1 mL min^{-1}, 10 MPa operating pressure. The GC was fitted with an RTX-5 column (30 m, ID 0.32 mm, film thickness, 0.25 μm), held at 40 °C for 1 minute, ramped at 17 °C/min to 280 °C and then held for 2 min. Quantification was performed by integration of the peak areas; response factors and conversions were calculated by the internal normalisation method. The products were identified by comparing the GC retention time with known standards and by GC–MS.

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