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Supercritical hydrogenation and acid-catalysed reactions “without gases”

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The high temperature catalytic decomposition of HCO_2H and HCO_2Et are used to generate the high pressure H_2 and the supercritical fluids needed for micro-scale hydrogenation of organic compounds; our approach overcomes the problems and limitations of handling high pressure gases on a small-scale and opens the way to the widespread use of continuous supercritical reactions in the laboratory.

The value of micro-scale reactors is becoming increasingly apparent.[1] The use of micro-reactors with supercritical fluids (SCFs) would be particularly useful on grounds of safety and environmental acceptability. Unfortunately, the marriage of SCFs and micro-reactors has been thwarted by difficulties in handling gases under high-pressure conditions on a very small scale. Here we describe a new approach in which the SCF and other gases are generated from liquid precursors, thus overcoming the problems of gas handling because delivering small quantities of liquids under high pressure is simple.

Supercritical hydrogenation, particularly in supercritical carbon dioxide, $scCO_2$, has several advantages over traditional solvent-based hydrogenation.[2–5] Mass transport limitations are minimised, and access to the catalytic centres can be enhanced. There is improved heat transfer, avoiding hot-spots, and SCFs are thought to increase catalyst lifetime by extracting residues from the surface of the catalyst.[6] These factors alone make SCF hydrogenation attractive, but the real advantage is the solvent-power of the SCF, which can be tuned by changes in both temperature and pressure.[5,7] Changing SCF conditions can alter the selectivity of reactions. The disadvantage, however, is the need for specialised equipment and bulky gas cylinders.

Miniaturisation of SCF equipment has the additional advantage of a faster response to changes in system conditions, with faster reaction optimisation. Furthermore, if gas cylinders could be eliminated, SCF chemistry would be transformed, becoming much more accessible to non-specialists.

Our solution to this problem is to generate both the CO_2 and H_2 needed for $scCO_2$ hydrogenation *in situ* by the catalytic decomposition of formic acid HCO_2H.[8,9] This is achieved by passing cold HCO_2H over a 5% Pt catalyst preheated to 450 °C, as shown schematically in Fig. 1.† Under these conditions the alternative decomposition products, CO and H_2O are only generated in relatively small quantities.[10]

This high pressure mixture of H_2 and CO_2 can be used for catalytic hydrogenation with a noble metal catalyst in reactor 2 (Fig. 1). The hydrogenation products can be collected directly from the back-pressure regulator, where phase separation between CO_2 and products occur. Table 1-1 shows that cyclohexene can be hydrogenated quantitatively in this way at 80 °C and 8 MPa, conditions similar to other $scCO_2$ hydrogenation methodologies.[2,11] Oct-1-ene, Table 1-2, can also be hydrogenated quantitatively to octane under similar conditions. However, as expected, oct-1-yne, Table 1-3, is fully hydrogenated to octane under these conditions.

Thus, the decomposition of HCO_2H is a practical means of performing supercritical hydrogenation as shown in Table 1. However the ratio of $CO_2 : H_2$ is fixed at 1 : 1. This is particularly unfortunate because we have previously shown that the control of H_2 concentration is the key to the success of SCF hydro-

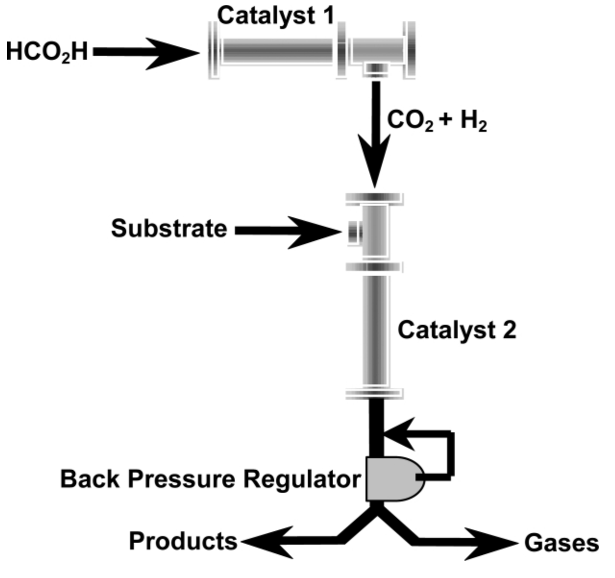

Fig. 1 Schematic experimental set-up. HCO_2H and organic substrate were delivered by HPLC pumps. System pressure was maintained by a back pressure regulator. For reaction conditions see Table 1.

Table 1 Results obtained from the “without gases” approach to SCF chemistry

Entry	Starting material	Product	%Yield[d]	Flow rate/ mL min^{-1} (HCO_2H)	Flow rate/ mL min^{-1} (HCO_2Et)	Tempera-ture/°C	Pressure/ MPa
1	Cyclohexene[a]	Cylohexane	100	0.4	0	80	8
2	Oct-1-ene[a]	Octane	100	0.4	0	80	8
3	Oct-1-yne[b]	Octane	100	0.4	0	80	8
4	*trans*-Cinnamaldehyde[b]	Hydrocinamaldehyde	91	0.4	0	200	20
5	Butane-1,4-diol[c]	Tetrahydrofuran	100	0	0.4	180	20
6	1,3,5-Trimethylbenzene[c]	1,3,5-Trimethylisopropylbenzene	45	0	0.4	200	10
7	*m*-Cresol[c]	3-Methyl-4-isopropylphenol	30	0	0.4	200	10

[a] Deloxan AP/II Pt (5%). [b] JM Supported Pd (2%). [c] Amberlyst-15. [d] All yields determined by GLC. All reactions were performed over a minimum of an 8 hour period without change in conversion or selectivity.

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genations.[2,5] We have overcome this limitation by exploiting the similar critical temperatures of CO_2 (31.1 °C) and C_2H_6 (32.6 °C) and generating mixtures of scCO_2 and scC_2H_6 by the catalytic decomposition of HCO_2Et, which leads to formation of CO_2 and C_2H_6.

The control of H_2 concentration is achieved by the parallel decomposition of HCO_2Et and HCO_2H over a single catalyst bed, to produced C_2H_6 and CO_2 and H_2 (Fig. 2). By controlling the relative flow rates of HCO_2H and HCO_2Et, a mixture of H_2 + CO_2 + C_2H_6 can be produced with the desired partial pressure of H_2.

Fig. 2 The key principle of the "without gases" approach to SCF hydrogenation. Changing the flow ratio of HCO_2H and HCO_2Et changes the concentration of H_2 in the SCF.

Thus by using two high pressure liquid pumps, we can achieve control of not only both the overall flow rate of the SCF solvent (a mixture of scCO_2 and scC_2H_6) but also the concentration of H_2 within that mixture. We demonstrate this control of the fluid by "titrating" H_2 into the fluid during the hydrogenation of oct-1-yne, Fig. 3.

Fig. 3 shows the effect of controlling H_2 concentration by this methodology. Oct-1-yne was hydrogenated whilst the flow rate of HCO_2H was increased to deliver the desired H_2 concentrations. It is important to stress that the two precursor liquids are decomposed over the same catalyst (either Pt or Pd). Therefore, tuning the concentration of H_2 does not increase the complexity of the apparatus unduly. We and other authors[12–14] have previously demonstrated that hydrogenation is possible in scC_2H_6 and, although the solvent properties of scCO_2 and scC_2H_6 will clearly be different, we believe that these differences are not so large as to mask the overall trends in the reactions.

The decomposition of HCO_2Et in the absence of HCO_2H opens up the possibility of SCF reactions other than hydrogenation. This is demonstrated in Table 1 entries 5–7. The dehydration of 1,4-butandiol to form tetrahydrofuran (THF) has previously been reported,[12] and interestingly the conversions obtained in the presence of a C_2H_6–CO_2 mixture appear to be slightly higher than in pure scCO_2, Table 1-5. Entries 6 & 7 show that the same approach works with acid-catalysed Friedel-Craft alkylations using propan-2-ol as the alkylating agent. Again the yields are comparable to previously reported alkylations in "pure" scCO_2.[15] These examples demonstrate that the "without gases" approach to SCF chemistry is versatile and provides a convenient methodology to anyone who wishes to experiment with SCFs.

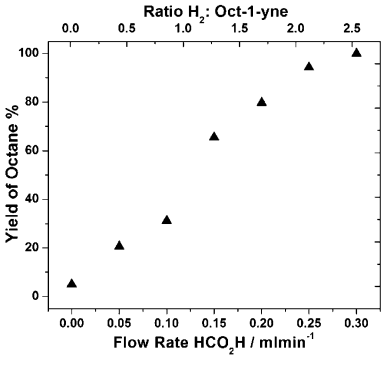

Fig. 3 Effect of increasing the relative concentration of H_2 on the hydrogenation of oct-1yne to octane.

There is one complication. The high temperature reverse water gas shift reaction is unavoidable. If uncontrolled, the concentration of CO in the gases generated will rise. However, the concentration of CO can be greatly reduced by using 90% HCO_2H in H_2O. The residual H_2O and CO do not appear to hinder unduly the fluid generated from being used as a hydrogenation medium, nor did they appear to deactivate/poison the catalyst significantly during the course of our experiments. Currently we are investigating how the presence of CO in the H_2/CO_2 mixture can be exploited for supercritical hydroformylation "without gases".

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Notes and references

† All equipment was constructed from 318-SS (SwageLok®) with HPLC pumps (Gilson 802) and a back pressure regulator (Jasco 880). HCO_2H (90%, Aldrich) and HCO_2Et (99.9%, Aldrich) and organic substrates were used as supplied. Pt 5% (7–10 g, reactor 1) was heated to 450 °C. The flow of HCO_2H and HCO_2Et was then started until system pressure was reached. Organic substrates were introduced after a period of *ca.* 30 min. after the system pressure stabilised. Samples were collected directly from the back pressure regulator and analysed by GLC.

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