# Partial oxidation of alcohols in supercritical carbon dioxide

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**Oxidation of water-insoluble alcohols in supercritical $CO_2$ over a Pd–Pt–Bi/C catalyst in a continuous fixed bed reactor affords high reaction rates and yields up to 98% of the corresponding ketones, aromatic and α,β-unsaturated aliphatic aldehydes, without the risk of using a flammable organic solvent.**

Partial oxidation of alcohols over supported platinum metal catalysts is an attractive, environmentally friendly process: air or oxygen can be used as oxidant in aqueous medium under mild conditions. Primary and secondary alcohols are readily oxidized to carboxylic acids and ketones, respectively, but partial oxidation of primary alcohols to aldehydes is limited to aromatic and α,β-unsaturated aliphatic alcohols where hydration and further dehydrogenation of the intermediate aldehyde is minor.[1–4] Drawbacks of the method are the frequently observed catalyst deactivation necessitating high catalyst–substrate ratio (20–50 mass%),[3,5] and the explosion risk in the case of readily dehydrogenating substrates.[6] Oxidation of water-insoluble alcohols is rather slow in organic solvents[7] and because of safety reasons the process is unattractive even on a laboratory scale.[5]

To overcome these restrictions, the organic solvent can be replaced by supercritical carbon dioxide ($scCO_2$),[8,9] *i.e.* $CO_2$ under conditions above its critical temperature ($T_c$ = 31.1 °C) and pressure ($p_c$ = 73.8 bar). Supercritical $CO_2$ has a number of distinct advantages over conventional organic liquid solvents, among which adjustable solvent strength and favorable transport properties are probably the most important. This medium is especially attractive for the oxidation of weakly polar, water-insoluble alcohols, due to the low polarity of $scCO_2$. Besides, $CO_2$ is relatively inert and non-flammable under oxidizing conditions. Products and solvent can easily be separated by releasing the pressure of the reaction mixture.

There are only two examples of the partial oxidation of alcohols with a solid catalyst in $scCO_2$ reported in the literature. Oxidation of methanol on iron oxide containing aerogels,[10] and ethanol on $Pt/TiO_2$,[11] affords the corresponding aldehydes in moderate yields (15–30%) compared to the conventional gas phase oxidation of small chain aliphatic alcohols.[12] Here we show that oxidation in $scCO_2$ is an excellent alternative to liquid phase reactions in organic solvents, affording the conversion of water-insoluble alcohols to (deactivated) carbonyl compounds at high rate and selectivity.

The experiments have been performed in a high-pressure continuous fixed bed reactor over a promoted noble metal catalyst (4% Pd–1% Pt–5% Bi/C).† It has been shown before that Bi or Pb promotion can remarkably enhance the performance of Pt and Pd.[4,5] For the study of the influence of reaction parameters, the conditions were chosen to achieve conversions in the range 2–10% in order to minimize the temperature gradients in the catalyst bed. In some cases the contact time and temperature were increased to achieve high conversions, though optimization of the reaction conditions was not attempted. These results, illustrating the potential of the method in the synthesis of activated and non-activated aldehydes and ketones, are collected in Table 1.

Octan-2-ol has been converted to octan-2-one with higher than 99.5% selectivity even at around 70% conversion. Only traces of oct-2-ene (by dehydration) and oct-4-ene (by dehydration and subsequent double bond migration) have been formed. The yield (68%) could be further increased by applying a higher amount of catalyst or lower mass flow rate. The octan-2-one yield increased exponentially with increasing temperature and approximately linearly with contact time. A bell-shaped curve was found for the effect of oxygen concentration in the feed (Fig. 1). The drop after the maximum in yield is attributed to the so-called over-oxidation of the catalyst, a phenomenon commonly observed with platinum metal catalysts.[3,5,6] The rate of oxidative dehydrogenation of alcohols is considerably higher on the reduced metal surface than on the oxygen-covered metal. Though oxygen is necessary to shift the alcohol–carbonyl compound equilibrium by oxidizing the hydrogen abstracted from the substrate, too high surface oxygen coverage reduces the overall reaction rate. An additional effect is the decreasing density of $scCO_2$ with increasing oxygen concentration, which may reduce the solubility of reactant and product. Changes in density of $scCO_2$ can also explain the influence of total pressure in the reactor. At constant temperature the yield reached a maximum at 110–120 bar.

Oxidation of octan-2-ol was relatively slow compared to the conversion of other secondary alcohols, such as 1-phenylethanol (Table 1). The transformation of 1-phenylethanol to acetophenone was nearly quantitative. Only traces of bis(1-

**Table 1** Selected examples of the partial oxidation of primary and secondary alcohols to carbonyl compounds in $scCO_2$. Catalyst: 4% Pd–1% Pt–5% Bi/C (3 g), feed flow rate 1.84 to 4.92 mol $h^{-1}$

| Alcohol | Oxygen/ mol% | Alcohol/ mol% | Butanone co-solvent/ mol% | *p*/bar | *T*/°C | Residence time/s | Yield (%) | Sel. (%) |
|---|---|---|---|---|---|---|---|---|
| Octan-2-ol | 4 | 2 | — | 110 | 140 | 17 | 68 | > 99.5 |
| 1-Phenylethanol | 2.7 | 2.7 | 5.3 | 110 | 140 | 13 | 95 | > 99.5 |
| 1-Phenylethanol | 5.3 | 2.7 | 5.3 | 110 | 140 | 13 | 98 | 99 |
| Octan-1-ol | 6 | 3 | — | 120 | 110 | 9.5 | 18 | 34 |
| Octan-1-ol | 2.5 | 5 | — | 95 | 80 | 25 | 11 | 82 |
| Benzyl alcohol | 2.5 | 5 | — | 95 | 80 | 13 | 26 | 99 |
| Benzyl alcohol | 2 | 2 | — | 120 | 100 | 9.5 | 65 | 78 |
| *p*-Anisyl alcohol | 2 | 2 | 4 | 120 | 110 | 9.5 | 70 | 87 |
| Cinnamyl alcohol | 4 | 2 | 4 | 120 | 110 | 9.5 | 78 | 98 |
| Cinnamyl alcohol | 4 | 2 | 8 | 120 | 110 | 9.5 | 61 | 96 |

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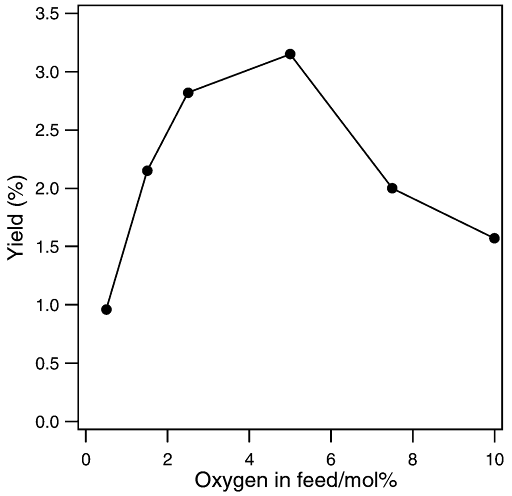

**Fig. 1** Effect of oxygen concentration in the feed on the yield of octan-2-one. Conditions: 100 °C, 95 bar, 2 g catalyst, 2.46 mol h$^{-1}$, 5 mol% octan-2-ol, rest $O_2$ and $CO_2$.

phenylethyl) ether were detected. In these reactions the solid substrate was dissolved in butanone for feeding, because the reactor tubes and valves were not heatable. Comparative experiments with octan-2-one indicated that the yield decreased with increasing amount of this co-solvent suggesting that its amount should be kept at a low level (Fig. 2). The change in reaction rate may be connected to H-bonding between the substrate and co-solvent. Formation of H-bonded species (clusters) can change the phase behavior in $scCO_2$.

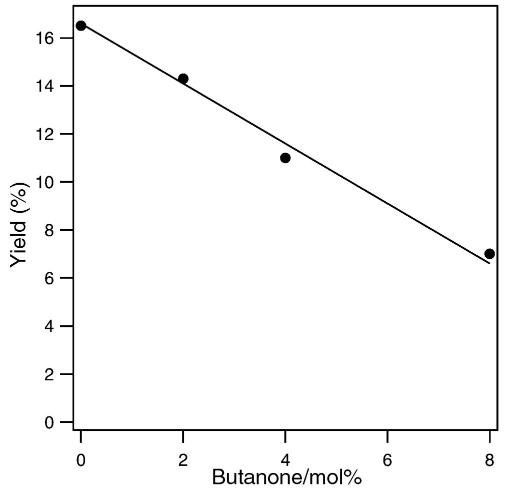

**Fig. 2** Dependence of octan-2-one yield on butanone concentration in the feed. Conditions: 120 °C, 120 bar, 2 g catalyst, 3.28 mol h$^{-1}$, 2 mol% octan-2-ol, 4 mol% $O_2$, rest $CO_2$.

Transformation of primary alcohols to aldehydes under similar conditions was fast but non-selective (Table 1). For example, octan-1-ol was oxidized to a mixture of octanal, octanoic acid and octyl octanoate. Oct-2-enal and dioctyl ether were produced in traces. Transient experiments indicated that the acid-catalyzed side reactions (ester and ether formation) were accelerated by the product octanoic acid. In general, the selectivity to octanal decreased rapidly with increasing conversion, especially at high temperature. Relatively good selectivity could be achieved by working at 60–80 °C and high contact time (Table 1). Still, the aldehyde yield was always less than 20%. For comparison, partial oxidation of primary aliphatic alcohols is non-selective also in aqueous medium,[4] due to the high reactivity of aliphatic aldehydes for hydration and subsequent rapid dehydrogenation.

Remarkably better selectivities can be achieved when the product aldehyde is stabilized by an aromatic ring or a C=C double bond. Benzyl alcohol was oxidized to benzaldehyde, benzoic acid and benzyl benzoate. Higher than 99% selectivity for benzaldehyde was obtained at 60–80 °C (Table 1). At 100 °C or higher the selectivity dropped below 80%. Clearly, good yields can be achieved only at moderate temperature and longer contact time (higher amount of catalyst and/or lower mass flow rate). Oxidation of *p*-anisyl alcohol to *p*-anisaldehyde afforded even better yields, presumably due to the electron-releasing methoxy group in the para position (Table 1).

The highest aldehyde yield with high selectivity was obtained in the oxidation of the $\alpha,\beta$-unsaturated alkylaromatic alcohol, cinnamyl alcohol. The negative impact of the co-solvent, used for dosing the solid substrate, is confirmed by the last two entries in Table 1. The aldehyde yield dropped from 78 to 61% when the alcohol was diluted with double the amount of butanone. Again, dosing of melted substrate can eliminate this complication.

From the results presented we can conclude that the aerobic oxidation of alcohols to carbonyl compounds in $scCO_2$ is a good alternative to the well-known aqueous phase oxidation on supported platinum metal catalysts. The present method has obvious advantages for the transformation of water-insoluble alcohols, avoiding the application of flammable organic solvents. Aqueous phase oxidations are typically performed at 40–90 °C for 3–10 h reaction time.[2–6] In the present study only 10–25 s residence time was necessary to achieve 65–98% yields of ketones, aromatic and $\alpha,\beta$-unsaturated aldehydes. The yields and selectivities may be further improved by applying longer residence times at relatively low temperature, and by direct dosing of melted substrates (without co-solvent). No catalyst deactivation or metal leaching was observed with time-on-stream. Generally, steady-state conditions were reached within 2–3 h. The limitation of the method is similar to that of the aqueous phase oxidation on platinum metal catalysts, namely that primary aliphatic aldehydes cannot be synthesized with good selectivity.

## Notes and references

† *Experimental procedure*: The reactions have been performed in a tubular flow reactor with an inner diameter of 13 mm and 38 ml volume. The alcohols were dosed by a Gilson 305 piston pump. Oxygen was supplied to the reactor using a six-port valve dosing 0.05 ml pulses at constant frequency. The constant pressure in the system was maintained by a backpressure regulator with $CO_2$. The total gas flow was controlled at the vent. The 4% Pd–1% Pt–5% Bi/C catalyst (CEF 196 RA/W, Degussa, BET surface area 930 m$^2$ g$^{-1}$) was reduced *in-situ* in hydrogen at 100 °C for 2 h prior to the kinetic measurements. For the parameter study the feed flow consisted of 5 mol% alcohol, 2.5 mol% oxygen and 92.5 mol% $CO_2$. 2 g catalyst was used, and a feed flow rate of 2.46 mol h$^{-1}$. The liquid products were separated from $CO_2$ and identified by GC and GC-MS. Yield and selectivities were determined by GC analysis using the internal standard method.

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