Continuous oxidation of benzyl alcohol in “supercritical” carbon dioxide

Gregor Jenzer, Tamas Mallat and Alfons Baiker *

Laboratory of Technical Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zurich, Switzerland
E-mail: baiker@tech.chem.ethz.ch

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“Supercritical” (dense) carbon dioxide has been applied as solvent for the partial oxidation of benzyl alcohol with molecular oxygen in a fixed-bed reactor. High rate and good selectivity to benzaldehyde (93–97%) has been achieved with 0.5 wt% Pd/alumina or 0.5 wt% Pd/C, at around 100 °C and 100 bar, using only moderate excess of oxygen. The by-product benzoic acid has an autocatalytic effect on the hydration of benzaldehyde, and the subsequent oxidative dehydrogenation leads to benzoic acid, and benzyl benzoate by esterification. Promotion of Pd by Pb improves the selectivity. No catalyst deactivation or metal leaching has been observed. The method provides reasonable yields at much lower temperature than that applied in conventional gas phase oxidation, showing a potential for the synthesis of thermolabile, water-insoluble aromatic aldehydes.

KEY WORDS: continuous fixed-bed reactor; oxidation; benzyl alcohol; benzaldehyde; Pd/alumina; “supercritical” carbon dioxide; oxygen

1. Introduction

Aerobic oxidation of alcohols to carbonyl compounds or carboxylic acids over Pt metals or Au has been thoroughly investigated in the past decades [1–5]. The reactions are generally carried out batchwise below 100 °C. The mild conditions and the aqueous medium are particularly well suited for the transformation of polyols and carbohydrates. Oxidation of water-insoluble alcohols may be carried out in the presence of a detergent [6], which additive, however, raises difficulties during work-up. Application of an organic solvent has also been proposed [7] but the explosion risk may hinder any practical application.

We have recently reported the application of “supercritical” carbon dioxide (scCO$_2$; $T_c = 31.1\,^\circ$C, $p_c = 73.8$ bar) as a substitute for organic solvents in liquid phase oxidation of alcohols [8]. Note that the widely used term “supercritical” is well defined only for pure substances, that is why we use the term between quotation marks. Dense, scCO$_2$ has a fair and tunable solubility for weakly polar, water-insoluble alcohols as well as for oxygen. It is a relatively inert and nonflammable solvent with high heat capacity. Despite of these and some other advantages, the potential of scCO$_2$ as solvent in partial oxidations is barely explored [9–13]. Partial oxidation of ethanol [14] in scCO$_2$ over Pt/TiO$_2$, as an alternative to gas phase oxidation, has already been attempted though the selectivity to acetaldehyde did not exceed 30%. We have also found that the Pt-metal-catalyzed aerobic oxidation of primary alcohols to (activated) aldehydes in scCO$_2$ is non-selective, similarly to the oxidation in aqueous phase [8].

Here we report the oxidation of an aromatic alcohol with molecular oxygen in “supercritical” CO$_2$ in a continuous fixed-bed reactor. The oxidation of benzyl alcohol to benzaldehyde has been chosen as a model reaction for the synthesis of (deactivated) aromatic aldehydes important in the field of fine and specialty chemicals.

2. Methods

The reactions have been performed isothermally in a tubular down-stream flow reactor with an inner diameter of 13 mm and 38 ml volume. Benzyl alcohol was dosed by a Gilson 305 piston pump. Oxygen was supplied to the reactor using a six-port valve dosing 0.05 ml pulses at high pressure and constant frequency. The constant pressure in the system was maintained by a pressure regulator with CO$_2$. The total gas flow was controlled at the vent.

The various supported Pd, Pt and Ru catalysts and their characteristics are listed in table 1. The reactions under standard conditions have been carried out with 5 g 0.5 wt% Pd/alumina (Engelhard 4586; cylindrical, 3.2 mm length and diameter), corresponding to a catalyst bed length of 5 cm and a space-time-related quantity W/F of 1.02 g h mol^{-1}, where W is catalyst weight and F the total molar flowrate. Glass beads (0.2 cm, 5 cm bed length) have been placed above the catalyst. The catalyst was reduced *in situ* by hydrogen at 100 °C for 2 h prior to the measurements. Standard conditions for the parameter study were 95 bar, 80 °C and the feed flow consisted of 5 mol% benzyl alcohol, 2.5 mol% oxygen and 92.5 mol% CO$_2$. This molar composition remained the same at all pressures. The liquid products were separated from CO$_2$ and analyzed by GC and GC-MS.

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* To whom correspondence should be addressed.

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Table 1
Comparison of structural and catalytic properties Pd, Pt and Ru catalysts (D = metal dispersion, S_{BET} = surface area).[a]

Catalyst	Code	S_{BET} ($m^2\,g^{-1}$)	D (%)	Conv. (%)	$S_{ald.}$ (%)	S_{acid} (%)	S_{ester} (%)
0.5 wt% Pd/alumina	Engelhard 5077	89	24[b]	13.5	95.6	0.1	4.8
0.5 wt% Pd/alumina	Engelhard 4586	96	29[b]	8.6	93.0	1.5	5.5
0.5 wt% Pd/alumina, 0.05 wt% Pb promoted		–	–	7.9	95.5	0.7	3.8
0.5 wt% Pd/carbon	Engelhard 5156	1220	17[c]	7.4	97.1	0.3	2.6
0.5 wt% Pt/alumina	Engelhard 1679	81	36[b]	0.3	100[d]	–	–
0.5 wt% Pt/alumina	Aldrich 20,601-6	103	43[b]	0.4	100[d]	–	–
0.5 wt% Ru/alumina	Engelhard 4871	96	7[b]	0.4	100[d]	–	–

[a] Conditions: 5 g catalyst, standard conditions.
[b] Determined by H_2 chemisorption.
[c] Determined by XRD line broadening.
[d] Aldehyde is the only detectable product at this low conversion.

Promotion of the 0.5 wt% Pd/alumina catalyst by lead was carried out by impregnation with an aqueous lead acetate solution, resulting in 0.05 wt% Pb content after drying *in vacuo* at room temperature and *in situ* reduction with gaseous H_2.

BET surface areas (S_{BET}) were obtained by physisorption of N_2 at 77 K using a Micromeritics ASAP 2000 instrument. Prior to measurement, the samples were outgassed to 0.1 Pa at 150 °C. Metal dispersion was determined by hydrogen chemisorption at 35 °C on a Micromeritics ASAP 2010C instrument. The samples were prereduced in H_2 at 350 °C and then evacuated at 0.1 Pa. The metal dispersion of a 0.5 wt% Pd/C (Engelhard 5156) was determined from X-ray line-broadening on a D-5000 Siemens diffractometer.

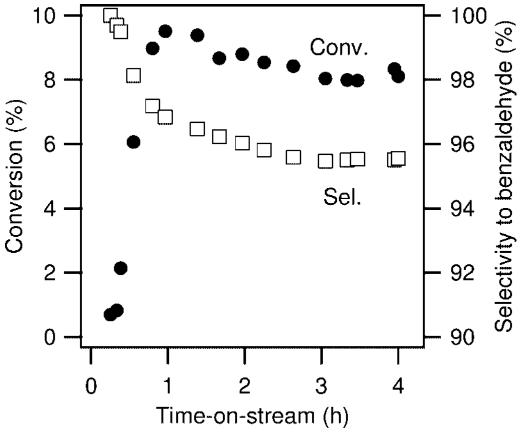
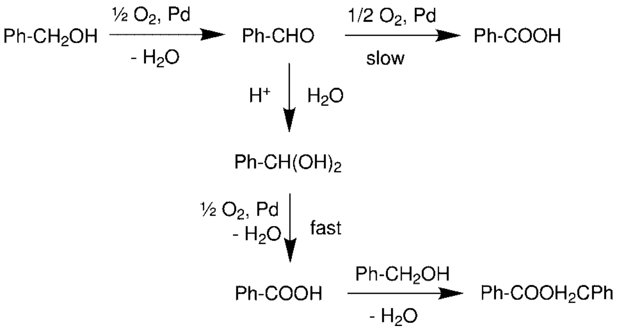


Figure 1. Initial transient behavior during oxidation of benzyl alcohol; 5 g 0.5 wt% Pd/alumina promoted by 0.05 wt% Pb, otherwise standard conditions.

3. Results and discussion

3.1. General features

Oxidation of benzyl alcohol over the 0.5 wt% Pd/alumina catalyst afforded benzaldehyde as the major product with over 90% selectivity. Conversion and selectivities reached steady state within 3 h time-on-stream, as illustrated in figure 1. The two by-products benzoic acid and benzyl benzoate formed by further oxidation, and subsequent esterification with the reactant alcohol, respectively (scheme 1). It is assumed that direct oxidation of the relatively stable (deactivated) benzaldehyde is slow and barely contributes to the formation of benzoic acid. The main route is the acid (or base)-catalyzed hydration with the co-product water, followed by the oxidative dehydrogenation of the hydrate [15]. The autocatalytic effect of the by-product benzoic acid (pK_a = 4.2) resulted in a loss of the overall selectivity with time-on-stream as seen in figure 1.



Scheme 1. Products formed in the oxidation of benzyl alcohol.

The Pt- or Pd-catalyzed aerobic oxidation of alcohols in aqueous medium is frequently accompanied by catalyst deactivation, and even leaching of the active component may be important [1–4]. Working in “supercritical” CO_2 we did not observe any significant deactivation or metal leaching. For example, the performance of the 0.5 wt% Pd/alumina catalyst was monitored for a period of 75 h time-on-stream (net working time). The parameters were varied in a broad range and the catalyst performance was tested repeatedly at 60 °C, 95 bar and $W/F = 1.02\ \mathrm{g\,h\,mol^{-1}}$. Under these conditions the conversion of benzyl alcohol remained in the range 4.8 ± 0.4% and no loss of activity was observed.

3.2. Influence of reaction parameters

The influence of some reaction parameters was investigated at relatively low conversions in order to minimize the temperature gradient in the catalyst bed. Raising temperature increased the conversion but lowered the aldehyde se-

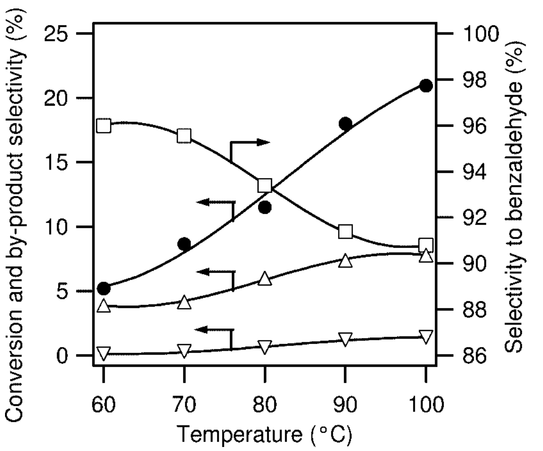


Figure 2. Effect of temperature on the reaction rate and product distribution: conversion (•), selectivities to aldehyde (□), acid (▽), and ester (△); standard conditions.

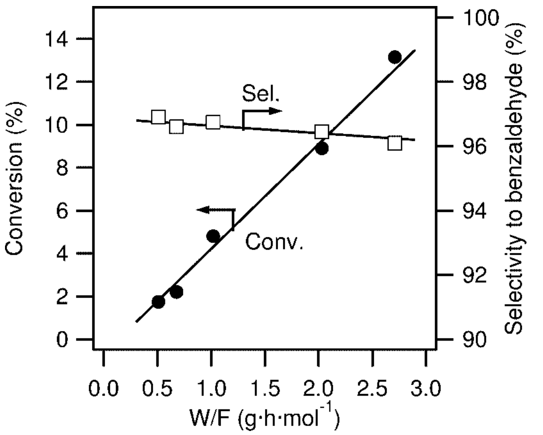


Figure 3. Conversion and benzaldehyde selectivity as a function of the space-time-related parameter W/F; 60 °C, otherwise standard conditions.

lectivity (figure 2). Further oxidation was especially important at temperatures above 100 °C. For example, 35% conversion was obtained at 130 °C under otherwise standard conditions, and the selectivities to aldehyde, acid and ester were 87.6, 2.4 and 10%, respectively.

The conversion of benzyl alcohol was linearly dependent on the space-time-related quantity W/F and the influence of this parameter on aldehyde selectivity was minor (figure 3).

The effect of oxygen concentration in the feed on the reaction rate is characterized by saturation-type curves (figure 4). At low oxygen concentration the rate drops to zero, indicating that the contribution of anaerobic oxidation of benzyl alcohol is negligible at this temperature. For comparison, dehydrogenation of benzyl alcohol over CuO required at least 250 °C to achieve good yields to benzaldehyde [16]. The decrease of benzaldehyde selectivity with increasing amount of oxygen in the feed was pronounced only at temperatures around 80 °C or higher. No catalyst over-oxidation (i.e., a drop in rate due to too high oxygen coverage on the metal surface [17,18]) was observed even at 7.5% O_2 in the feed, corresponding to 300% of the stoichiometric ratio for quantitative transformation of benzyl alcohol to benzaldehyde. The likely explanation is the facile oxidation of benzyl alcohol, and the absence of strongly adsorbing by-products. As concerns the latter point, the good solubilizing power of $scCO_2$ may be crucial in removing by-products from the metal surface.

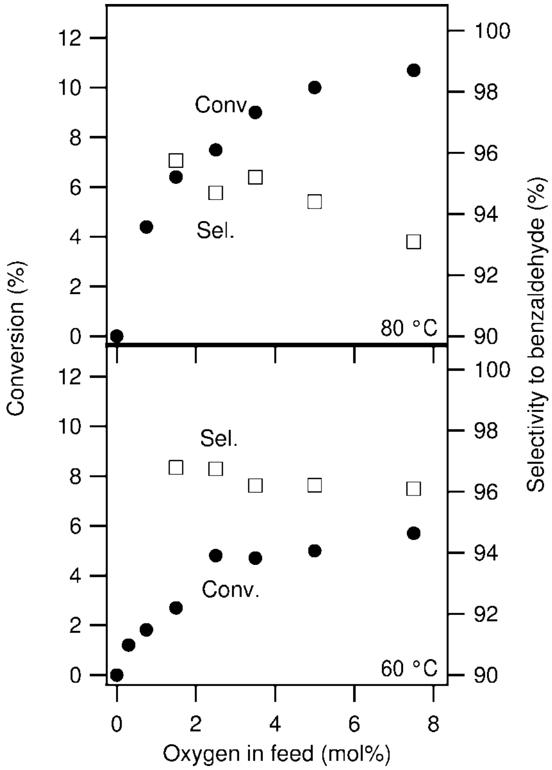


Figure 4. Effect of oxygen concentration in the feed: (top) at 80 and (bottom) at 60 °C; otherwise standard conditions.

The influence of total pressure on the rate and selectivity of oxidation is rather complex and strongly depends on the set of other parameters, such as the temperature (figure 5). The highest conversion was achieved at 100–115 bar and the aldehyde selectivity was either constant or even increased with raising pressure. An explanation of these effects would require the knowledge of the phase behavior under reaction conditions but no data are available in the literature on the CO_2–O_2–benzyl alcohol–benzaldehyde system.

3.3. Comparison of Pt group metal catalysts and the influence of promotion

A comparison of some supported Pd, Pt and Ru catalysts revealed that Pd is far the best catalyst for benzyl alcohol oxidation in $scCO_2$ (table 1). The nature of support (alumina or carbon) and the Pd dispersion (17–29%) are of secondary importance: the aldehyde selectivity was always in the range 93–97% and the highest difference in conversion was less than a factor of 2.

It was attempted to improve the performance of palladium by promotion with lead. When using a 0.05 wt% Pb–0.5 wt% Pd/alumina catalyst the selectivity to by-products decreased from 7 to 4.5%, with only a small drop in activity (table 1). The assumption that one adsorbed Pb atom occu-

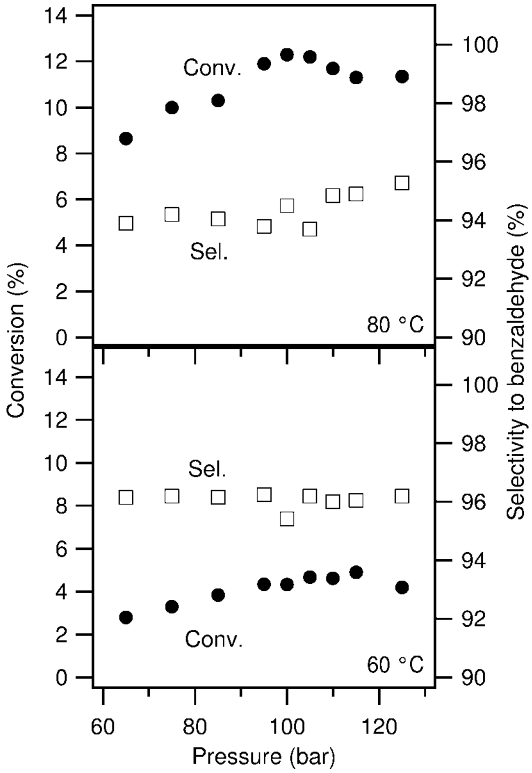


Figure 5. Influence of total pressure on the catalyst performance: (top) at 80 and (bottom) at 60 °C; otherwise standard conditions.

pies two surface Pd atoms [19], and all promoter atoms are located on the Pd surface, leads to an upper limit of 27% surface coverage of Pd by the lead promoter.

We have carried out some non-isothermal experiments involving a significant temperature gradient in the catalyst bed. These experiments confirmed that conversion of benzyl alcohol can be increased without any loss in aldehyde selectivity. For example, 96% benzaldehyde selectivity was achieved at 56% conversion with the 0.5 wt% Pd/alumina catalyst at around 100–120 °C (other conditions: 120 bar, $W/F = 3.79\ \mathrm{g\,h\,mol^{-1}}$, 10 mol% O_2, 5 mol% alcohol). The limit to further increasing the conversion in this highly exothermic reaction was the insufficient rate of heat transport in the reactor used.

To our knowledge, continuous vapour phase oxidation of benzyl alcohol on a broad range of different catalysts afforded at best 96% selectivity to benzaldehyde. Perovskite oxides [20–22] and Au [23] provided this selectivity at 48–50% conversion, at atmospheric pressure and ca. 350–450 °C. Obviously, the Pd-catalyzed oxidation in $scCO_2$, at high pressure but relatively low temperature, has a potential in the synthesis of non-volatile or thermally labile aromatic aldehydes important in fine chemistry. The major advantage of oxidation in dense CO_2, compared to liquid phase oxidation in acetic acid [24] or n-heptane [7], is the elimination of the explosion risk.

4. Conclusions

We have shown that only Pd has good activity and selectivity in the aerobic oxidation of benzyl alcohol to benzaldehyde in "supercritical" CO_2. A 0.5 wt% Pd/alumina catalyst has been stable without any sign of metal leaching or deactivation within 75 h time-on-stream. Though the conditions have not yet been optimized, the method offers clear advantages compared to liquid phase, or high temperature gas phase, oxidation processes in the synthesis of aromatic aldehydes.

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