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# Selective oxidation of benzyl alcohol to benzaldehyde in “supercritical” carbon dioxide

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## Abstract

The selective oxidation of benzyl alcohol to benzaldehyde with molecular oxygen in “supercritical” carbon dioxide over a commercial 0.5 wt.% $Pd/Al_2O_3$ catalyst has been studied in a continuous flow fixed-bed reactor. Optimization of the reaction conditions afforded a high turnover frequency (TOF) of 1585 $h^{-1}$ at 80 °C and 150 bar, with a rather constant selectivity around 95%. Parameter studies showed a strong dependence of the catalyst activity on temperature and oxygen concentration. Phase behaviour studies indicated that the increase in activity, which resulted in the high TOF, could be traced back to the fact that the reactor was operated under single phase conditions. High pressure in situ XAS uncovered that the palladium constituent was mainly in a reduced (metallic) state during alcohol oxidation, and that it was quite easily reduced and re-oxidized at 80 °C by the reactants, alcohol and oxygen, respectively.

*Keywords:* Selective oxidation; Benzyl alcohol; Supercritical carbon dioxide; *In situ* X-ray absorption spectroscopy; Phase behaviour

## 1. Introduction

Noble metal catalysed oxidation of alcohols and carbohydrates in an aqueous medium with molecular oxygen is a technique widely used in the synthesis of speciality and fine chemicals possessing carbonyl or carboxylic groups [1–4]. The technique is attractive from both economic and environmental point of view: oxygen is a cheap and easily available oxidant and water is the only co-product. For water insoluble alcohols the use of a detergent [5] or of an organic solvent [6] have been proposed. Another attractive solution is to carry out the reaction in “supercritical” $CO_2$ [7–11]. The term “supercritical” is used here between quotation marks because it can be well defined only for pure substances [8,12]. “Supercritical” $CO_2$ has distinct advantages over conventional solvents. In particular, dense $CO_2$ is a relatively cheap, non-flammable and nontoxic medium with tunable solubility for weakly polar alcohols [7]. In addition, the relatively high heat capacity of $scCO_2$ is advantageous during these exothermic reactions. These advantages, together with the use of molecular oxygen, may lead to a safer and cleaner process.

Despite of these advantages little has been done in this field [8]. Only recently, studies on the oxidation of higher alcohols were reported. Jenzer et al. studied the oxidation of octyl alcohols and of benzyl alcohol in a continuous flow system [12,13]. Steele et al. reported on the oxidation of different alcohols, among which there were also solid alcohols, in a batch reactor [14]. Also the oxidation of 1- and 2-propanol was recently studied in a batch reactor [15]. In this work the oxidation of benzyl alcohol to benzaldehyde has been chosen as a model reaction and the performance was studied as a function of different process variables. To gain a deeper fundamental insight into the reaction system, phase behaviour and in situ spectroscopic studies were performed, using a view cell and X-ray absorption spectroscopy (XAS).

## 2. Experimental

### 2.1. Catalytic measurements

The reactions have been performed isothermally in a tubular reactor with an inner diameter of 13 mm and 38 ml volume. The temperature of the catalyst bed was monitored by means of an axially movable thermocouple placed in the centre of the reactor [12]. A commercial shell impregnated

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catalyst consisting of 0.5 wt.% $Pd/Al_2O_3$ (Engelhard 4586) was used as a sieved fraction (ca. 0.5–1.4 mm). The metal dispersion determined by hydrogen chemisorption was 0.29. Pure alumina of the same sieved fraction was used to dilute the catalyst bed, in order to avoid possible hot spot formation by the exothermic reaction. The catalyst was pre-reduced with $H_2$ before starting the measurements. Benzyl alcohol (Fluka, 13 160, purity >99.0%) was dosed by a Gilson 305 piston pump and oxygen (Pangas, purity ≥99.999%) was supplied to the reactor through a six-port valve dosing 0.05 or 1 ml pulses at high pressure and constant frequency. The constant pressure was maintained by a pressure regulator with $CO_2$, and the total gas flow was controlled at the vent. Quantitative results were obtained via GC analysis (HP-6890, FFAP column).

### 2.2. *Phase behaviour studies*

The phase behaviour of the system under reaction condition was investigated in a computer controlled high pressure view cell, equipped with on-line digital video imaging. Details on this apparatus can be found elsewhere [16]. In order to prevent $O_2$ exposure of the view cell, experiments were performed using nitrogen instead of oxygen. These two gases have in fact similar polarity and molecular mass, and their critical points are far from that of $CO_2$. Therefore, it is possible to assume that a dilute mixture of oxygen and nitrogen in $CO_2$ behaves similarly.

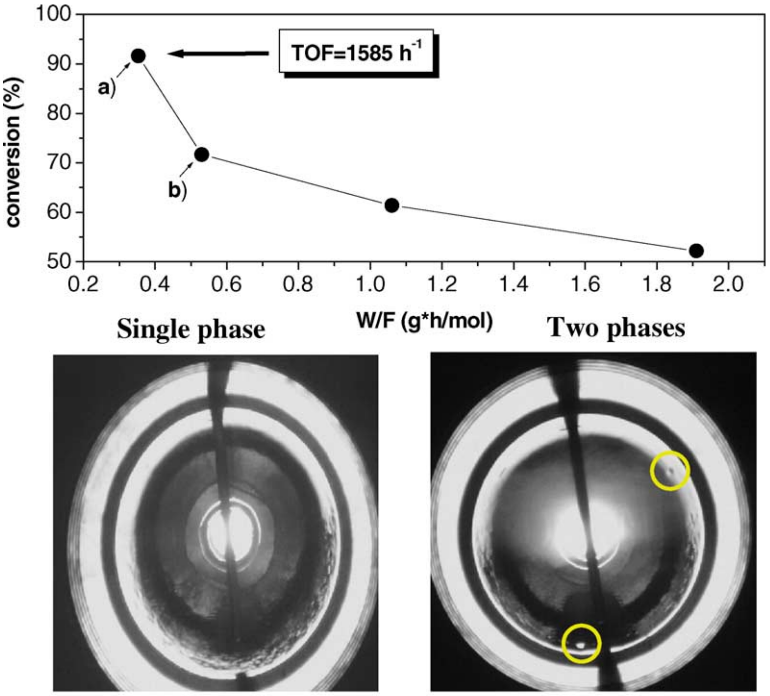
### 2.3. *XAS measurements*

In situ XAS experiments were performed in a specially constructed cell [17] at the Hamburger Synchrotronlabor (HASYLAB at DESY, Germany) at beamline X1 using a Si(311) double crystal monochromator. EXAFS spectra were recorded around the Pd K-edge in the step scanning mode between 24 320 and 24,500 eV. The raw data were energy-calibrated, smoothed, background corrected and normalized using the WINXAS 2.1 software [18].

## 3. Results and discussion

The selective oxidation of benzyl alcohol over 0.5 wt.% $Pd/Al_2O_3$ performed at sufficiently high temperature (>70 °C) and high pressure (>100 bar) afforded benzaldehyde with very good TOF and with a selectivity around 95%.

As depicted in Fig. 1, an exceptionally high TOF of 1585 $h^{-1}$ (conversion: 0.108 $mol_{alc}$/h, Pd on the surface: $6.81 \times 10^{-5}$ mol) was obtained by increasing the $CO_2$ flow rate. Since the reactant feed and the alcohol/oxygen ratio were kept constant, the $CO_2$-flow increase corresponds to a decrease of the reactant concentrations. Varying the $CO_2$ flow rate from 0.04 to 0.233 mol/min thus results in a decrease of the reactant concentrations for the alcohol from 4.68 to 0.86 mol% and of the space–time related parameter



(a) (b)

Fig. 1. Effect of space–time related parameter (*W*/*F*) on benzyl alcohol conversion, obtained by variation of $CO_2$ flow rate. Conditions: 150 bar, 80 °C, 5 g 0.5% $Pd/Al_2O_3$, 0.002 mol/min alcohol, 0.001 mol/min $O_2$; Snapshot a: phase behaviour at $P = 150$ bar, $T = 80\,^{\circ}C$ of the mixture: 0.43% $O_2$, 0.86% alcohol, 98.71% $CO_2$; Snapshot b: phase behaviour at $P = 150$ bar, $T = 80\,^{\circ}C$ of the mixture: 0.65% $O_2$, 1.3% alcohol, 98.05% $CO_2$.

$W/F$ from 1.91 to 0.35 g h $mol^{-1}$(Fig. 1, $W$ is the catalyst weight and $F$ is the total molar flow rate). For comparison, the liquid phase oxidation of benzyl alcohol was performed in toluene using a flow through cell under similar conditions. In this case a TOF of 20 $h^{-1}$ was obtained. Also in literature lower values of TOF are generally reported for the liquid phase oxidation [19–21]. Parallel phase behaviour studies uncovered that in the region where this high TOF was obtained (alcohol = 0.86 mol%), the reaction mixture was present as a single phase (snapshot a in Fig. 1), while for higher alcohol concentration (1.3 mol%) the development of a separate liquid phase was observed (snapshot b in Fig. 1). This is an example proved by the drops of liquid present on the window and at the bottom of the view cell (marked in snapshot b). Hence, the increase of conversion with $CO_2$ flow rate in Fig. 1 can be traced back to a change in the phase behaviour of the reaction mixture towards an ideal single “supercritical” phase, in which the gas–liquid mass transfer resistance is lowered. Even under the conditions of maximum conversion, the temperature profile along the catalyst bed was almost flat. This behaviour is attributed to the dilution of the catalyst with alumina and to the relatively high $CO_2$ heat capacity that renders this solvent particularly suited for exothermic reactions.

Conversion as a function of temperature is depicted in Fig. 2. Also in this case the curves are measured by varying the $CO_2$ flow rate. A marked dependence of the activity from the temperature is observed, and especially passing from 70 to 80 °C leads to a consistent increase of the conversion. Phase behaviour studies (not reported) showed a decrease of the overall density of the mixture with temperature, and a consequent decrease of the fraction of reacting liquid dissolved in the $CO_2$ [22,23]. This behaviour could counteract the activity increase with temperature. However, in the present case the effect of temperature on reaction rate seems to play a more important role than the influence of the density change of $CO_2$ on solubility of reactants. XAS measurements (not shown) evidenced that reduction of Pd by the reactant alcohol (metallic Pd is regarded as active phase in the reaction [1,2]) starts taking place only at temperature above 70 °C. Therefore, this could be a possible explanation of the considerably higher activity recorded at 80 °C.

Benzyl alcohol oxidation as a function of oxygen concentration is depicted in Fig. 3. In order to avoid a total conversion of the alcohol, a smaller amount of catalyst (diluted with alumina) was used. Fig. 3 shows that the rate ($r$) of alcohol oxidation as function of oxygen concentration is different if the concentration of the reactants in $CO_2$ is varied. For the higher concentration of reactants in the feed and thus a low $CO_2$ flow rate (0.1 mol/min), an initial increase of activity with oxygen was found, followed by a strong decrease. The maximum is at about 6 mol% of oxygen in the feed. Phase behaviour studies revealed a decrease of the overall density of the reaction mixture with increasing $O_2$ concentration. Over the whole region the mixture was present as two phases. The initial increase of activity could thus be attributed to the fact that more $O_2$ is dissolved in the alcohol/$CO_2$ phase. Interestingly, two regions with high alcohol oxidation rate were found at low concentration of the reactants in the feed (higher $CO_2$, 0.233 mol/min). Again a maximum is found at 6% oxygen, but additionally the TOF is high at low $O_2$ concentrations. Phase behaviour studies uncovered that only at low $O_2$ concentration ($c(O_2) \approx 0.43\%$) the mixture is present as a single phase. Hence, oxygen and alcohol are present in the same phase leading to an optimum catalytic activity. The increase of activity in the two

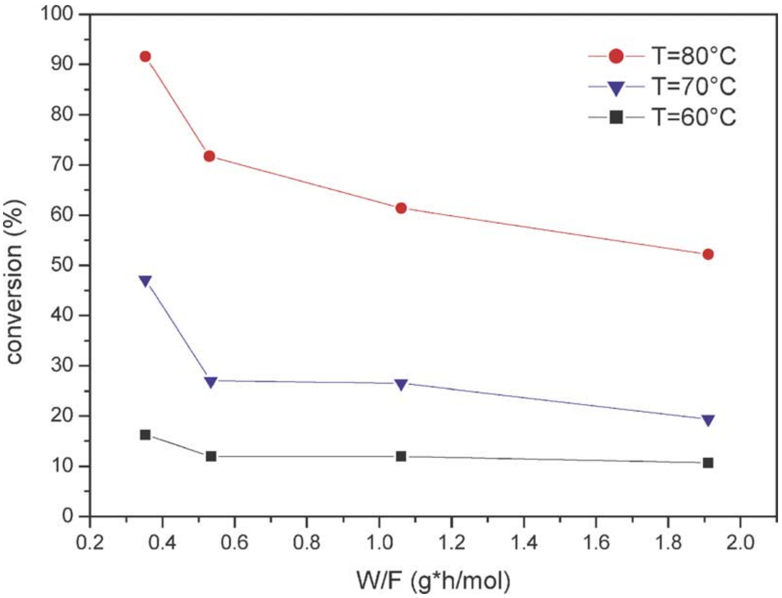


Fig. 2. Conversion of benzyl alcohol as a function of the space–time related parameter ($W/F$) at 60, 70 and 80 °C (150 bar, 5 g 0.5% Pd/$Al_2O_3$, 0.002 mol/min alcohol, 0.001 mol/min $O_2$).

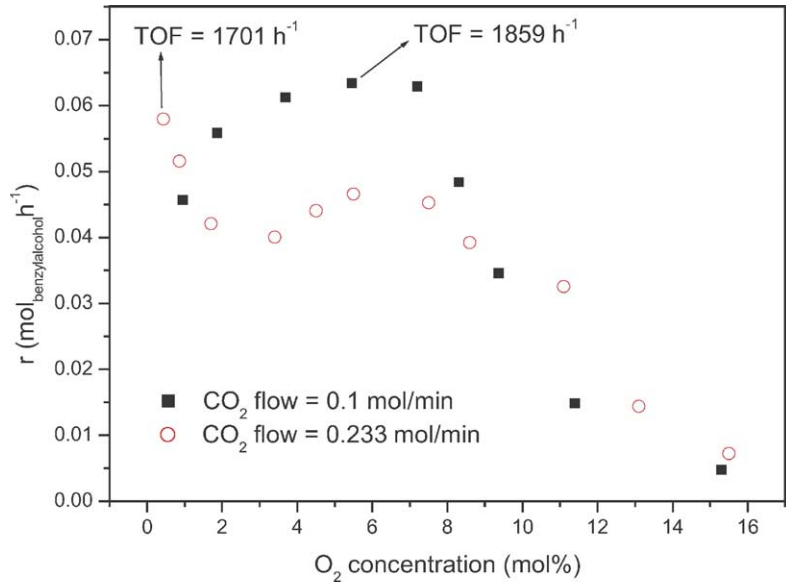


Fig. 3. Rate ($r$) of benzyl alcohol oxidation as a function of the oxygen concentration in the feed for two different $CO_2$ flow rates (150 bar, 80 °C, 2.5 g 0.5% Pd/$Al_2O_3$, 1.5 g alumina, 0.002 mol/min alcohol).

phase region is similar to the first case and a decrease in activity is found for both flow rates. One possible explanation for the decrease of activity at higher oxygen concentration could be the oxidation of palladium, which is known from liquid phase oxidation to play an important role in the reaction [2,4,24]. In order to tackle this question, XAS measurements were performed under reaction conditions. Some results are shown in Fig. 4, detailed results are reported elsewhere [17]. Spectrum 1 in Fig. 4 is the catalyst before reduction, and according to the near edge structure of the Pd K-edge, the palladium constituent is in a nearly fully oxidized state. Spectrum 3 corresponds to the catalyst after reduction and under reaction conditions (150 bar, 80 °C, total flow of 0.11 mol/min, alcohol 1.89%, oxygen 0.95%). The near edge structure reveals that the catalyst is mainly in a reduced state. However, comparison with the catalyst after reduction in $H_2$ (not shown) uncovered that tiny changes had occurred, and that the catalyst was not completely reduced. The TOF measured under these conditions was 1518 $h^{-1}$. Increasing the oxygen concentration to 1.89% led to an increase of the activity (TOF 1894 $h^{-1}$), but nearly no changes in the structure were observable. Spectrum 2 was recorded after stopping the alcohol feed, and therefore with the catalyst in a dense $O_2/CO_2$ fluid (1.89% $O_2$). Comparison with the catalyst under reaction conditions (spectrum 3 in Fig. 4) shows that a partial oxidation of the palladium constituent

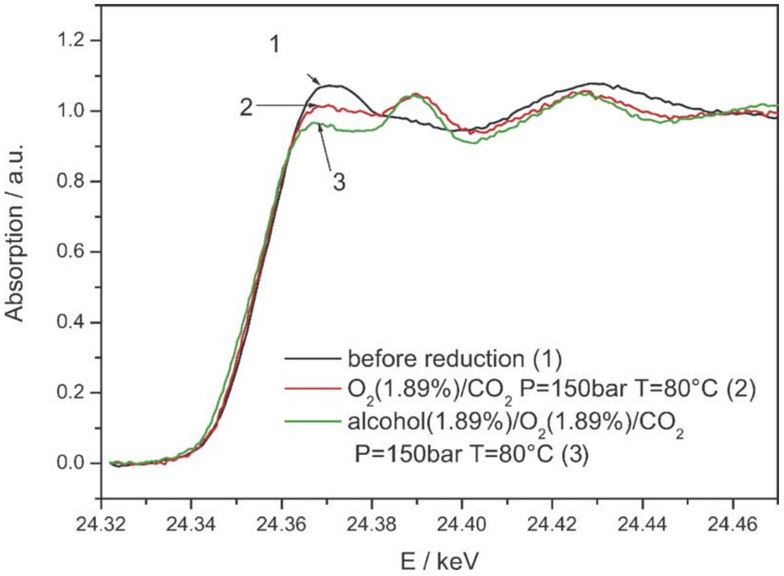


Fig. 4. XAS spectra of 0.5% Pd/$Al_2O_3$ around the Pd K-edge before reduction, under reaction conditions and during re-oxidation (details in text).

occurred. Re-adding the alcohol lead again to reduction of the catalyst, but not to the same extent as at the beginning. Also the catalytic activity was lower (TOF is only $1504\,h^{-1}$ at 1.89% $O_2$). The same type of experiment performed in the conventional reactor gave similar results, where the TOF changed from $1761\,h^{-1}$ before treatment to $1441\,h^{-1}$ after treatment with oxygen. Nevertheless, the activity could be almost completely restored with longer time on stream. These experiments uncovered that the palladium constituent is mainly in a reduced (metallic) state during alcohol oxidation. $PdO_x$ on the surface of the Pd particles deactivates the catalyst and is probably responsible for the decrease of activity above 8% $O_2$ in Fig. 3. This behaviour supports speculations in literature according to which Pd in the reduced state is most active [1,2,12,15,24]. In contrast to our investigations in liquid phase [24], we observed here that the palladium constituent in dense $CO_2$ is not completely reduced under optimum conditions.

## 4. Conclusions

This work shows that the partial oxidation of benzyl alcohol to benzaldehyde in $scCO_2$ can be performed with high TOF by optimizing the reaction conditions. Phase behaviour of the reaction mixture and oxidation state of the palladium constituent were found to be crucial for high catalyst activity. These are the key factors to be considered when optimizing the catalytic performance of the system.

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