**Continuous catalytic oxidation of solid alcohols in supercritical CO₂:
A parametric and spectroscopic study of the transformation of
cinnamyl alcohol over Pd/Al₂O₃**

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Abstract

Cinnamyl alcohol was oxidized to cinnamaldehyde in a continuous fixed-bed reactor with molecular oxygen over an alumina-supported palladium catalyst in supercritical carbon dioxide modified with toluene. A strong dependence of the reaction performance on pressure and oxygen concentration in the feed was found. Optimization of the reaction conditions resulted in a higher catalytic activity than in liquid phase. At 120 bar, 80 °C, and double stoichiometric oxygen concentration, a turnover frequency of 400 h⁻¹ at a selectivity of 60% to cinnamaldehyde was achieved. Spectroscopic investigations and the knowledge of the selectivity pattern turned out to be crucial for a deeper understanding of the reaction allowing a rational optimization. Under almost all experimental conditions (even at high oxygen concentration) hydrogenated by-products, stemming from internal hydrogen transfer reactions, were detected in the effluent. This indicated that alcohol dehydrogenation is the first reaction step, further confirmed by spectroscopic investigations. *In situ* XANES and EXAFS uncovered that in the whole experimental range investigated the palladium constituent was mainly in a reduced state and that its surface could be oxidized only in the absence of cinnamyl alcohol in the feed. Bulk phase behaviour studies and investigations at the catalyst/fluid interface, performed by visual inspection and combined transmission and ATR-IR spectroscopy, uncovered that the reaction performed best in the biphasic region. Moreover, cinnamaldehyde and carbon dioxide but hardly any toluene and cinnamyl alcohol were detected inside the porous catalyst, evidencing a strongly different product composition inside the porous catalyst compared to the bulk phase.

Keywords: Aerobic oxidation, cinnamyl alcohol, supercritical CO₂, phase behaviour, *in situ* ATR-IR, *in situ* EXAFS, *operando* spectroscopy;

Introduction

Supercritical carbon dioxide is a well-suited solvent for oxidation reactions due to its natural abundance, non-toxicity and inertness, which result in safer operations. Moreover, it is fully miscible with molecular oxygen (air) and exhibits high heat capacity [1-10]. Compared to most conventional solvents, the use of supercritical CO₂ results also in an improved internal and external mass transport leading often to an enhancement of the global reaction rate. This is especially valid when single phase conditions are present [1, 2, 9, 11, 12].

Among heterogeneously catalyzed oxidation reactions, the selective oxidation of alcohols to the corresponding aldehyde or ketone is important in fine chemistry [13-16]. The reactions are typically performed under mild conditions over noble metal supported catalysts, using water as a solvent and molecular oxygen or air as the sole oxidant. For weakly polar alcohols, poorly soluble in water, the use of supercritical CO₂ has been proven to be beneficial, avoiding the use of detergents or organic solvents [17, 18]. This leads to a safer and more environmentally friendly process. In several cases, higher rates and selectivity than in conventional solvents with improved catalyst lifetime were reported [17-21]. The reactions were performed either in a batch reactor or in a continuous fixed-bed reactor in a wide temperature and pressure range. Optimal reaction conditions often significantly depend on the catalyst, on the substrate and also on the reactor type. Only recently, deeper spectroscopic insight into such oxidation reactions has been gained [17, 20, 22, 23]. Significantly different features compared to liquid phase oxidation were evidenced, but up to now these kinds of studies are limited.

In fine chemical industry, many of the commercially interesting alcohols are solid. Only a few studies on the selective oxidation of solid alcohols using supercritical CO₂ as a solvent have been reported [18, 21] and discontinuous reactors (batch reactors) were applied. Here we propose a simple approach to continuously oxidize solid alcohols with molecular oxygen in supercritical

CO₂. The method consists in dissolving the solid alcohol in a small amount of a liquid organic solvent and to continuously feed it as a reaction mixture via a liquid pump. One of the advantages is the flexible setup that allows continuous processing of both liquid and solid alcohols without losing the technical and environmental benefits of supercritical CO₂ (non-flammability, process intensification, improved mass and heat transfer). Moreover the alcohol can be easily dosed and possible blocking of tubing and valves can be prevented due to the use of a co-solvent.

In the focus of the present work was the oxidation of the solid and technically relevant cinnamyl alcohol (scheme 1). The influence of the main process variables (pressure, temperature, co-solvent amount, oxygen concentration) on the reaction rate and on the product/by-product distribution has been studied. In previous studies we have shown that a profound knowledge of the phase behavior, the solid/fluid interface and the structure of the catalysts is of vital importance for reactions in supercritical fluids [9, 12, 20, 23]. Moreover, even in liquid phase controversial discussions on the nature of the active site and the reaction mechanism exist [13, 14, 16, 24, 25]. Both oxidized palladium and metallic Pd sites have been speculated to be the active species in the reaction.

Hence, complementary to the catalytic activity measurements, *in situ* spectroscopic studies are required for a rational process optimization, and we applied here both *in-situ* infrared spectroscopy (in transmission and attenuated total reflection (ATR) mode) combined with video monitoring and *in-situ* X-ray absorption spectroscopy (XAS). While the IR/visual inspection studies could give insight into the phase behavior of the reaction mixture and the phenomena taking place at the catalyst/fluid interface during the reaction, XAS was used to gain insight into the catalyst structure under reaction conditions. Additional insight into the reaction mechanism was gained by the selectivity pattern observed during the cinnamyl alcohol oxidation since the substrate can undergo different side-reactions (scheme 2) [24, 26].

Experimental

Catalytic measurements: The reactions have been performed isothermally in a fixed-bed stainless steel 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 center of the reactor. A commercial shell impregnated catalyst consisting of 0.5 wt % Pd/Al₂O₃ (Engelhard 4586) was crushed and used as a sieved fraction (ca. 0.5-1.4 mm). Pure alumina (Engelhard 43299) of the same sieved fraction was used to dilute the catalyst bed, in order to avoid possible hot spot formation by the exothermic reaction. 2.5 g of catalyst and 1.5 g of alumina were loaded, corresponding to a bed length of ca. 4 cm. Glass beads were placed above the catalyst to ensure an optimal distribution of the reactants at the entrance of the catalytic bed. The catalyst was pre-reduced with H₂ before starting the measurements in order to improve its stability and guarantee that it was initially completely reduced. Cinnamyl alcohol (Fluka, 96330, purity ≥ 97.0%) and toluene (Fluka, 89681, purity > 99.7) were used as received. Typically 10 g of cinnamyl alcohol (melting point 30-33°C, technical purity) were dissolved in 100 ml of toluene (corresponding to a molar concentration of toluene of 1.9%, shown *e. g.* in Figure 1), with the exception of experiments in which the amount of toluene was varied in order to check its influence on the reaction performance. The cinnamyl alcohol/toluene mixture was fed to the reactor by a Gilson 305 HPLC pump with a volumetric liquid flow of 0.482 ml/min, resulting in an alcohol molar flow rate of $3.55 \cdot 10^{-4}$ mol/min. Oxygen (Pangas, purity ≥ 99.999%) was supplied through a six-port switching valve (Rheodyne, model 7000) dosing 0.05 or 1 ml pulses at high pressure and constant frequency. The constant pressure was maintained by a pressure regulator with CO₂, and the total gas flow was controlled at the vent. Product identification was performed by GC/MS

(HP-5973), and quantitative results were obtained via GC analysis (HP-6890, FFAP column). Details on the experimental setup can be found elsewhere [17].

FTIR and phase behaviour measurements: Infrared spectroscopic investigations were carried out in a custom-made stainless steel high-pressure view cell (SITEC AG), which withstands pressures up to 200 bar and temperatures up to 200 °C. A sapphire window covering the entire diameter allows visual observation and digital imaging of the bulk phase behaviour. The cell is additionally equipped with IR transmission windows (ZnSe, Komlass, diameter 8 mm, length 19.2 mm) that allow transmission IR measurements in the upper part of the reactor (path length of 0.4 mm). An internal reflection element (IRE, Komlass, made of ZnSe, trapezoidal shape, angle of incidence 60°, length 27 mm, height 2 mm, depth 10 mm) mounted at the bottom of the hollow cylinder allows ATR-IR measurements. A motor driven carriage moves a set of mirrors that directs the light beam either to the IRE, or to the transmission windows, thus allowing quasi-simultaneous transmission IR and ATR-IR measurements. Fourier transform infrared (FTIR) spectra were recorded with a Bruker Optics IFS-66/s spectrometer equipped with a liquid nitrogen-cooled MCT detector, typically accumulating 200 scans at a resolution of 4 cm⁻¹. The experiments were performed in the following way: at first the alcohol with toluene were loaded, then CO₂ was fed into the cell at 40 °C and finally the desired pressure was adjusted by heating to 80 °C and change of the volume. The pressure was increased from 120 to 160 bar and then back again to 120 bar while recording both transmission IR and ATR-IR spectra after each pressure change of 5 bar. Detailed descriptions of a similar experimental setup and of the experimental procedure can be found in refs. [23, 27]. To coat the IRE with a thin catalytic layer, 5 mg of 5 wt % Pd/Al₂O₃ (Johnson-Matthey, 324) was suspended in 0.5 ml water. The suspension was put onto the crystal, which was then dried over night in air at room temperature.

XAS measurements: *In situ* XAS experiments were performed in a specially constructed flow cell (details in ref. [22]) at the Hamburger Synchrotronlabor (HASYLAB at DESY, Germany) at beamline X1 using a Si(311) double crystal monochromator. The crystals were slightly detuned to minimize higher harmonics and three ionization chambers filled with Ar were used to record the intensity of the incident and transmitted X-ray. A Pd reference foil was used for energy calibration. EXAFS spectra were recorded around the Pd K-edge in the step scanning mode between 24000 and 25600eV. The raw data were energy-calibrated, smoothed, background corrected and normalized using the WINXAS 3.0 software [28]. The k^3 -weighted EXAFS data were Fourier transformed in the interval $k = 2.7 - 13 \text{ \AA}^{-1}$. The *in situ* flow cell warrants optimal conditions for the simultaneous monitoring of both the catalyst structure and the catalytic activity [22]. The catalyst and the substrate/solvents utilized during the *operando* XAS measurements were the same as used during the catalytic experiments in the conventional reactor. Cinnamyl alcohol conversion and the selectivity to cinnamaldehyde were determined by GC analysis (HP-6890, FFAP column).

Results

Catalyst and co-solvent screening

The selective oxidation of cinnamyl alcohol to cinnamaldehyde (scheme 1) was performed in a continuous flow reactor using supercritical CO₂ as a solvent and molecular oxygen as oxidant. The solid cinnamyl alcohol was dissolved in a fixed amount of organic co-solvent and then fed to the reactor as a liquid solution in a continuous way. As a first preliminary step, a screening to identify the best catalyst and a suitable co-solvent was performed using always the same activation procedure. The catalysts were tested during one day and the results are reported in

Table 1. Palladium supported on alumina turned out to be the only active catalyst. In addition, performing the reaction with cinnamyl alcohol dissolved in toluene showed a better performance than in acetone and THF, both in terms of conversion and selectivity to the aldehyde. Therefore, all further investigations were performed over a 0.5 wt % Pd/Al₂O₃ using toluene as a co-solvent.

Reaction performance in toluene modified dense CO₂

As a next step the effect of toluene concentration on the reaction performance was investigated, and the results are reported in Fig. 1. A constant reaction rate was found when increasing the toluene amount from 1 to 2.9 mol %, with an alcohol conversion of *ca.* 15% and an increasing selectivity with the amount of co-solvent. Higher amounts of toluene resulted in a lower activity (conversion *ca.* 5% at 15.4 mol % toluene), even though the selectivity to the aldehyde kept on increasing. On the basis of these results, it was decided to perform the parametric study presented in this work at concentration of toluene of 1.9 mol %, which seems to represent a good compromise between amount of toluene added, catalytic activity and selectivity to the aldehyde. Note that at a lower toluene concentration of 1 mol % unstable conditions of the setup were observed, with the CO₂ flow rate slightly oscillating around the desired value. This was probably due to the formation of solid substances in the expansion valves, which could be avoided by applying higher amount of co-solvent. The use of “co-solvents” [29-31] or “expanded liquids” [32, 33] has also been used in other studies in order to overcome solubility limitations [34, 35] and in general to tune the solvent properties of SCFs without spoiling their advantageous properties [36, 37]. In some cases higher reaction rates than in neat CO₂ were reported, indicating that the co-solvent may play a crucial role affecting phase behaviour, mass transfer properties and adsorption/desorption phenomena [29-31, 38]. Also in the present case a similar role of the co-solvent cannot be excluded, and therefore toluene should probably not be regarded only as a

mean to dissolve the solid alcohol. In principle other solutions to process the solid cinnamyl alcohol alone, without the use of a co-solvent, could be used, *e. g.* the injection of a melted alcohol or the saturation method. However, these solutions would have required a more complex experimental setup for dosing the alcohol and to prevent possible formation of solid deposits.

Catalyst deactivation

In contrast to previous studies on the selective oxidation of benzyl alcohol in scCO_2 , in case of cinnamyl alcohol the palladium catalyst showed during the first working days a significant deactivation, with the alcohol conversion in a standard experiment dropping from 60% at the first day to 14.9% at the fifth day. Instead, the selectivity to cinnamaldehyde increased from 72% to 79%. An increase of selectivity with a decrease of conversion has been observed in other sets of experiments as well, and it can be considered as a general feature of this reaction under the reaction conditions typically applied in the present study. Interestingly, after *ca.* 5 working days, no further deactivation was observed and the catalyst showing steady state behaviour was used for the parametric studies.

Reaction network

During the catalytic tests, different by-products were detected in the effluent and identified by GC/MS. By-products originating from hydrogenation, hydrogenolysis, decarbonylation and carbon-carbon double bond cleavage were observed, but only some of them were present in appreciable amount and thus taken into account in the reaction network shown in scheme 2. The number appearing in brackets after the product name will be referred to in the following parts of the work.

Systematic catalytic investigations

On the basis of the previous results, a parametric study was performed over a stabilized 0.5 wt % Pd/Al₂O₃ catalyst using toluene as a co-solvent. The influence of the total pressure on conversion and selectivity to cinnamaldehyde is reported in Fig. 2a. In the region of low pressure a slight increase of conversion with pressure was observed. A maximum was reached at 120 bar, with the turnover frequency (TOF) increasing up to 400 h⁻¹. At 130-140 bar, a sharp drop of the conversion was found, with a TOF of 90 h⁻¹ at 150 bar. This behaviour is opposite to previous observations for benzyl alcohol [23], and it will be discussed later in the light of phase behaviour and X-ray absorption spectroscopy results. The selectivity to cinnamaldehyde instead constantly increased with pressure, showing a more marked jump between 130 and 140 bar, corresponding to the drop of the reaction rate. At 120 bar, where the maximum reaction rate was observed, the selectivity to cinnamaldehyde was 58.4%. In Fig. 2b the product/by-product distribution is shown, uncovering that the main product cinnamaldehyde is always present in the highest concentration. In the region of low pressure (corresponding to the higher catalytic activity measured) the two hydrogenated by-products, 3-phenyl-1-propanol (2) and beta-methylstyrene (5), are present in comparable amount to cinnamaldehyde (1).

Another important variable that has a strong impact on the reaction performance is the oxygen concentration in feed. Two sets of experiments at 120 and 150 bar were performed varying the oxygen concentration up to 10 mol % (Figs. 3 and 4). In a test performed without feeding oxygen, a similar catalytic activity was measured at 120 bar (conversion of cinnamyl alcohol 12.4%) and 150 bar (conversion 13%), with a rather different selectivity to cinnamaldehyde (57.6% at 120 bar vs. 79% at 150 bar). The dehydrogenation via internal hydrogen transfer seems to be dominant, as also indicated by the by-product distribution. At 120 bar, the hydrogenated products 3-phenyl-1-propanol (11.2%) and beta-methylstyrene (30.9%), and at 150 bar mainly 3-

phenyl-1-propanol (19.2%) were detected. Adding oxygen (0.15 mol %, same concentration of the alcohol) resulted in a marked increase of the reaction rate at 120 bar (Fig. 3a), with the alcohol conversion increasing from 12.4% to 58.7%, with an almost unchanged selectivity to the aldehyde. The by-product distribution slightly changed showing an increased production of 3-phenyl-1-propanol (2) and a decreased production of beta-methylstyrene (5). Increasing the oxygen concentration up to 10 mol % did not result in a clear trend, showing at first a slight increase of the conversion with the oxygen concentration up to 1.2%, and then a slight deactivation. However, no strong deactivation like the one observed during benzyl alcohol oxidation [22] was measured, and at 10 mol % O₂ in the feed the cinnamyl alcohol conversion was still 51.4%. The selectivity to cinnamaldehyde increased with increasing oxygen amount (Fig. 3). At 10 mol %, the product/by-product distribution showed cinnamaldehyde (82.2%), benzaldehyde (11.7%) and 3-phenyl-1-propanol (3.6%). Generally, with increasing oxygen partial pressure the amounts of the hydrogenated by-products 2 and 5 decreased, while the oxygenated by-product benzaldehyde (4) increased. This is a striking result and indicates the higher availability of surface oxygen on the palladium active sites.

On the contrary, addition of 0.15 mol % oxygen at 150 bar (Fig. 4) did not boost the reaction rate, and compared to the “oxygen free” experiment, conversion and selectivity to cinnamaldehyde remained more or less unchanged. As Figure 4 shows, an increase of the oxygen concentration resulted first in a decrease (at 1.2 mol %), followed by a marked increase of the catalytic activity. The conversion jumped from 6.4% (at 1.2 mol % O₂) to 62% (at 7.6 mol % O₂). A further increase to 10 mol % O₂ in feed led only to a slight deactivation, which is smaller than in case of benzyl alcohol [20, 22]. At 10 mol % the measured cinnamyl alcohol conversion was 53% and the selectivity to cinnamaldehyde was 72.9%. The by-product distribution indicated the

predominance of the oxygenated products, but still some internal hydrogen transfer was observed (20% of benzaldehyde vs. 5.2% of 3-phenyl-1-propanol and traces of beta-methylstyrene).

Phase behaviour studies

The phase behaviour of the reaction mixture was studied by means of video recording combined with transmission IR spectroscopy of the bulk supercritical phase and ATR-IR spectroscopy of the liquid phases. A similar approach was previously used in the case of benzyl alcohol, demonstrating that, in addition to the phase behaviour, also information on the phase composition can be gained [23]. The variation of the toluene amount had only little effect on the transition from the biphasic to the monophasic region of the reaction mixture. For four different compositions (1 mol %, 1.9 mol %, 7.7 mol %, 15.4 mol % toluene in 0.15 mol % alcohol/0.15 mol % O₂/CO₂) we observed the transition to a single supercritical phase between 120 and 130 bar. Below 120 bar, where the highest activity was measured, all the mixtures were present as biphasic systems. This can be for example seen in the snapshots reported in Fig. 5 taken while investigating the phase behaviour of the mixture containing 7.7 mol % toluene. An increase of the pressure by *ca.* 4 bar resulted in a sharp transition from a two phase region at 126.4 bar (Fig 5, snapshot a), via an intermediate region with an higher volume of the CO₂-expanded toluene phase at 128.7 bar (Fig 5, snapshot b) to a single phase region at 130.6 bar (Fig. 5, snapshot c). This phase transition can be best visualized by a movie provided as electronic supplementary information. The phase behaviour of the 1.9 mol % toluene containing mixture, which was the one used in the parametric study, was additionally studied by means of ATR-IR spectroscopy because of the small amount of liquid present in the cell. The results are reported in Fig. 6. The transition to a single supercritical phase in the bulk started at 120 bar, as shown by the decrease in intensity of the cinnamyl alcohol bands at 730 and 692 cm⁻¹ and the shift to higher wavenumber

of the ν_2 -band of CO_2 (660 cm^{-1} at 115 bar, 662 cm^{-1} at 120 bar, spectrum 1 compared to spectrum 2). The shift of the ν_2 -band in the dense liquid like phase is due to the interaction of CO_2 with the alcohol [23, 39], but no alkylcarbonic acids were found in significant amounts [40]. However, at 130 bar and after a long equilibration time, the bands of alcohol were still visible (spectrum 3), and to fully dissolve the substrate a higher pressure was necessary. At 150 bar the bands of alcohol could hardly be detected (spectrum 4), as a consequence of the very short path length of the probing beam in the ATR-IR technique. However, under single phase conditions, the ATR-IR signals reflect only the data that can also be extracted from the transmission IR results. These observations indicate a slower transformation than the sudden one observed for the mixture containing 7.7 mol % toluene (Fig. 5), but also in this case, at 120 bar the mixture was still present as two phases.

Investigations at the catalyst/fluid interface by ATR-IR spectroscopy

In-situ ATR-IR studies at the solid/fluid interface of the Pd-catalyst were performed by coating the ATR crystal with a layer of active catalyst with the aim to gain information on the phase behaviour inside the catalyst pores and on the interactions between CO_2 , toluene, substrates and the solid catalyst. Simultaneously, the reaction progress was monitored by transmission IR spectroscopy. The reaction conditions applied resembled as closely as possible the ones encountered during the catalytic tests in the continuous flow reactor. In addition, experiments were performed in a manner that the spectroscopic data and the catalytic activity were reported at the same time, leading to real *in situ* investigations.

Interestingly, in the presence of a catalyst layer hardly any band of cinnamyl alcohol or toluene was detected in the ATR-IR spectrum (Fig. 7) and the carbon dioxide ν_2 band was not shifted like in the liquid-like bulk phase. Hence, the situation is similar to the single, supercritical bulk phase.

This may be due to the higher virtual pressure inside narrow pores which is known to lead to a shift of the critical temperature ([41-43]) and we therefore describe the behaviour inside the porous catalyst as “supercritical” although it is well-known that the critical parameters are only clearly defined in case of pure substances [1, 9, 11]. In summary, in the catalyst pores the supercritical conditions that are observed above 150 bar in the bulk phase were reached at lower pressure and temperature.

Cinnamyl alcohol was then oxidized over the palladium catalyst at 120 bar and 80 °C in the batch reactor infrared view cell (0.15 mol % alcohol, 0.15 mol % O₂, 1.9 mol % toluene, 97.8 mol % CO₂). With increasing reaction time in the ATR-IR spectra recorded at the catalyst/fluid interface there is an increase of the cinnamaldehyde C-O stretching band at 1683 cm⁻¹ (Fig. 8), while for the whole reaction time hardly any band of alcohol was detectable. At the end of the reaction (after *ca.* 280 min) the band of cinnamaldehyde was quite intense, indicating that the aldehyde was not fully dissolved in the bulk supercritical phase but remained in the catalyst pores as well. Two intense bands at 3134 and 3215 cm⁻¹ also appeared, which may be assigned to by-products containing probably carboxylic groups. Performing the reaction at 150 bar resulted in a lower reaction rate, in line with the observation during the catalytic tests, and during the whole reaction time bands of aldehyde or alcohol were hardly visible in the ATR-IR spectra. At the end of the reaction (after *ca.* 680 min) two intense bands at 3128 and 3222 cm⁻¹ appeared (not shown), which were very similar to the ones observed at 120 bar and therefore probably belong to similar types of by-products. The conversion of cinnamyl alcohol in the batch reactor at 120 and 150 bar as a function of reaction time and calculated from the area of the cinnamaldehyde C=O stretching band is shown in Fig. 9. These measurements were taken while investigating the phenomena at the catalyst/fluid interface and are in good accordance with the catalytic results described above. Experiments performed at 120 bar without adding toluene (not shown) resulted in a lower

catalytic activity, underlining the beneficial role of the co-solvent, which thus cannot only be regarded as a mean to dissolve the solid alcohol. The phenomena at the solid/fluid interface instead did not remarkably differ from the ones observed in the presence of toluene.

XAS experiments

Operando X-ray absorption experiments were performed in order to shed more light on the oxidation state of the palladium catalyst during cinnamyl alcohol oxidation and to investigate whether the measured changes in activity could be traced back to modifications of the catalyst structure. The X-ray absorption spectroscopic data were measured under the reaction conditions where the catalytic activity showed the main changes. Note that the experimental setup was projected and developed in order to mimick as closely as possible at the synchrotron the experiments performed in the home laboratory [22]. Therefore the reaction conditions applied during the XAS investigations are exactly the same (with respect *e. g.* to pressure, temperature, CO₂ flow, reactants concentration) as those usually applied in the conventional experiments. The spectra, focussed on the XANES region are reported in Fig 10a, the corresponding Fourier transformed EXAFS spectra in Fig. 10b. The catalyst was at first reduced in 5% H₂/He at 100 °C (spectrum 1) and then exposed to a CO₂ flow (0.233 mol/min) at 120 bar and 80 °C, resulting in a slight reoxidation of the palladium constituent, indicated by the decrease in intensity of the Pd-Pd backscattering at 2.75 Å (Fig 10b, spectrum 2). Cinnamyl alcohol (0.15 mol %), dissolved in toluene (1.9 mol %), was then added, but almost no change was observed in the EXAFS spectrum (not shown), while instead a remarkable catalytic activity was measured (Table 2). Adding also oxygen (0.15 mol %) resulted in a further slight decrease of the Pd-Pd backscattering (Fig 10b, spectrum 3). The reaction proceeded readily also in the EXAFS flow cell (Table 2), and a TOF of 265 h⁻¹ was measured, in line with the investigations in the conventional reactor (Fig.

3), emphasizing the proximity to real *operando* studies. Increasing the oxygen concentration to 7 mol % resulted in a lower catalytic activity with an improved selectivity to cinnamaldehyde (Table 2), but the EXAFS spectrum remained almost unchanged (not shown). Increasing the pressure to 150 bar (at 0.15 mol % oxygen), thus reaching single phase conditions in the bulk supercritical phase, did not have any detectable effect on the catalyst structure, as shown by spectrum 4, which presented very similar features to spectrum 3, both in the XANES region (Fig. 10a) and in the Fourier transformed EXAFS spectra (Fig. 10b). As expected the catalytic activity dropped, and a TOF of 91 h^{-1} was achieved under these conditions. Increasing the oxygen amount to 7 mol % at 150 bar resulted in a higher activity, with the TOF rising to 234 h^{-1} , once again in agreement with the measurements performed in the conventional fixed-bed reactor (Fig. 4). Also at 7 mol % of oxygen in the feed no remarkable changes in the oxidation state of the palladium constituent could be observed, except for a further slight decrease of the Pd-Pd backscattering (spectrum 5 in Fig. 10b). Stopping the alcohol feed thus leaving the catalyst in 5% O_2 in CO_2 at 150 bar and 80°C , finally resulted in an oxidation of the palladium constituent. This can be clearly seen by the decrease of the Pd-Pd feature at 24.39 keV in the near edge region of the X-ray absorption spectrum (Fig 10a, spectrum 6) confirmed also by the remarkably less intense Pd-Pd backscattering in the Fourier transformed EXAFS spectrum (Fig. 10b, spectrum 6). Interestingly under these conditions also the Pd-O backscattering could be clearly observed at 1.5 Å. Fitting results showed that the Pd coordination number decreased from about 7 to 6 ($R = 2.75 \text{ Å}$) and the oxygen coordination number amounted to about 2 ($R = 1.98 \text{ Å}$).

Discussion

Cinnamyl alcohol was oxidized by molecular oxygen – for the first time in a continuous way – over a palladium catalyst in supercritical carbon dioxide. The reaction rate is significantly higher

than in conventional organic solvents ([16, 44] and references therein). A strong dependence of the reaction rate on pressure and oxygen concentration was found (Figs. 2-4), with a high performance achieved in the low pressure region (90-120 bar) and at high oxygen concentration (5-8 mol %). However, the selectivity pattern and the spectroscopic investigations indicate different reaction pathways in these two regions of high catalytic performance, which were not observed in liquid phase oxidation [45].

The influence of pressure on the reaction rate can be traced back to the characteristic phase behaviour of the reaction mixture (Fig. 5). At low pressure two phases were present in the bulk, with a CO₂-rich gas-like phase (containing also part of the cinnamyl alcohol and almost all the toluene) in equilibrium with an alcohol-rich liquid-like phase (Figs 5 and 6). The higher activity in the biphasic region of the bulk phase behaviour is opposite to that reported for benzyl alcohol [20, 23] and clearly shows that the transition to a single bulk phase has a negative influence on the reaction rate. Hence, gas-liquid transfer is not rate limiting. Whereas the bulk phase is present at 120 bar as a biphasic reaction mixture with a dense liquid-like phase probably in contact with the catalyst particles (as suggested by the ATR-IR investigations performed without coating the catalyst on the crystal), ATR-IR spectroscopy performed by coating the crystal with a layer of an active catalyst suggests that the conditions inside the pores resemble the situation found in the bulk phase under single phase conditions (*e. g.* rich in carbon dioxide). This situation is schematically shown in Fig. 11. A liquid-like phase in the bulk is probably beneficial since it leads to a higher alcohol concentration around the particles and because it exhibits a higher solvation power, beneficial for the extraction (desorption and transport) of the aldehyde and the by-products, including water. Note that cinnamaldehyde was observed inside the porous catalyst (cf. Fig. 8) while this was not the case for benzaldehyde that can also be well dissolved by supercritical carbon dioxide [23, 46].

The selectivity pattern under these conditions indicates a high concentration of hydrogen on the catalyst surface. In fact, alcohol oxidation over noble metal catalyst proceeds via oxidative dehydrogenation, the first step being the adsorption and the dehydrogenation of the alcohol to the corresponding aldehyde or ketone [16, 47]. The formed hydrogen can be removed either by oxidation with molecular oxygen [45] or in the case of cinnamyl alcohol also by internal hydrogen transfer [48], as indicated in Fig. 11. The high catalytic activity at oxygen free conditions and 3-phenyl-1-propanol (2) as the main by product both in the presence and in the absence of oxygen, unravels that the reaction readily proceeds by internal hydrogen transfer and that hydrogen is available on the catalyst surface in high concentration. This also favours hydrogenolysis reactions, as shown by the high concentration of beta-methylstyrene (5) in the effluent. Interestingly, despite of the high concentration of surface hydrogen, propylbenzene (from the hydrogenation of the C=C double bond of beta-methylstyrene) was detected only in traces. Higher amounts of beta-methylstyrene than in liquid phase oxidation were found [24, 45] and this difference can probably be traced back to its higher affinity for scCO₂. As soon as it is formed, it quickly desorbs and diffuses out of the catalyst pores without further reaction.

The increased reaction rate at 150 bar and high oxygen concentration (5-8 mol %, Fig. 4) may be attributed to a change of the bulk phase behaviour, since the reaction mixture becomes biphasic at high O₂ amount, as expected due to the decrease of the overall density [49]. The phase composition/behaviour inside the catalyst pores remained instead unvaried. Again, two phases in the bulk phase and supercritical-like conditions inside the catalyst pores led to a high catalytic activity. The reaction pathway at high oxygen concentration is different, as indicated by the by-product distribution, which showed benzaldehyde as the main by-product. Benzaldehyde can be formed from cinnamic acid by oxidative cleavage of the carbon-carbon double bond. The reaction is known in literature, although it requires severe reaction conditions with strong

oxidants ([50-52] and references therein). In the present case the reaction may be favoured by the fast removal of benzaldehyde due to its high solubility in supercritical carbon dioxide [23, 46, 53], which continuously shifts to benzaldehyde the equilibrium of the reaction. Although cinnamic acid was only observed in traces during the catalytic tests, carboxylic species were detected at the catalyst fluid interface by infrared spectroscopy (Fig. 8). It may be formed by the acid catalyzed hydration with the co-product water of cinnamaldehyde, followed by the oxidative dehydrogenation of the hydrate [54]. Interestingly in the experiment performed at 120 bar, benzaldehyde could be observed as the main by-product only above 5 mol % of oxygen in the feed, while at 150 bar it was the main by-product already at *ca.* 1 mol % of oxygen. This may once again be traced back to the bulk phase behaviour. At 150 bar supercritical conditions in the bulk implies an improved external mass transfer and therefore a higher oxygen concentration at the catalyst surface. From previous results [31] we can exclude that benzaldehyde may be derived from oxidation of toluene. Typically the reaction takes place at higher temperature [55, 56].

Oxygen has thus a strong influence on the phase behaviour and on the reaction pathway, but in contrast to previous observation with benzyl alcohol [20, 22] it did not play a direct role in catalyst deactivation. Up to 10 mol % of oxygen in the feed no strong deactivation could be observed (Figs. 3 and 4). In principle, deactivation due to over-oxidation may take place when the oxygen supply on the catalyst is higher than its consumption by the reactions, thus leading to a surface oxidation of the palladium constituent [14, 16, 24, 57, 58]. In the present case no deactivation due to over-oxidation of the catalyst surface was observed due to the high concentration of surface hydrogen available under all the reaction conditions investigated. *In situ* XAS studies support this conclusion. Under almost all the experimental conditions investigated the palladium constituent was found to be in an almost fully reduced state during alcohol oxidation. Since an increase of the pressure from 120 to 150 bar (at 0.15 mol % of oxygen in the

feed) resulted in no changes in the catalyst structure, we can exclude the possibility that the liquid-like phase present in the bulk protected the catalyst from being over-oxidized, *e.g.* by lessening the diffusion rate of oxygen. Also at high oxygen concentration (7 mol %) no remarkable oxidation of the palladium constituent could be observed (Fig. 10). Interestingly, only when the alcohol feed was stopped thus leaving the catalyst in 5 mol % O₂/CO₂, an evident oxidation of the surface palladium took place. This underlines the role of surface hydrogen in preserving the catalyst from being oxidized and evidences that the dehydrogenation step readily proceeds. The results are also well in agreement with the observed by-product distribution, particularly of the hydrogenolysis products. The internal hydrogen transfer is a very sensitive probe for Pd-H species on the surface. Also at high oxygen concentration, despite the fact that benzaldehyde became the major by-product, 3-phenyl-1-propanol (2) and 3-phenyl propionaldehyde (3), deriving from internal hydrogen transfer (scheme 2), were still present in considerable amount, showing that even under these conditions hydrogen is still available on the palladium surface.

Conclusions

A simple and effective method for the continuous selective oxidation of solid cinnamyl alcohol in supercritical carbon dioxide over a heterogeneous palladium catalyst has been presented. The use of toluene as a co-solvent allowed performing the reaction efficiently and in a continuous manner. Upon optimization, a high reaction rate with a TOF of 400 h⁻¹ and selectivity to cinnamaldehyde around 60% was achieved. A marked dependence on pressure and oxygen concentration was found. Depending on the different reaction conditions, hydrogenation, hydrogenolysis, oxidative cleavage of carbon-carbon double bonds were observed as side reactions. Phase behaviour studies, *in situ* transmission and ATR-IR spectroscopy as well as

operando XANES/EXAFS studies were excellent tools to gain a deeper insight into the reaction mechanism, the solid/fluid interface and the state of the catalyst. The oxidation reaction is significantly different to benzyl alcohol oxidation in supercritical carbon dioxide. In contrast to benzyl alcohol oxidation, a biphasic reaction mixture was beneficial for the catalytic performance of the Pd-catalysed oxidation of cinnamyl alcohol, and no deactivation due to oxygen in high concentration was observed. Both the reaction network and the *in situ* XANES and EXAFS studies under reaction conditions uncovered that Pd was mainly in metallic state, even in the presence of high amounts of oxygen. In addition, IR-spectroscopic studies at the solid-fluid interface evidenced that the phase composition was significantly different in the catalyst pores than in the bulk phase, particularly under reaction conditions. This shows that a good understanding of the fluid or reaction mixture inside a porous catalyst is inevitable at near- or supercritical conditions.

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Electronic Support Information available

A movie recorded while investigating the phase behaviour of a 0.15 mol % alcohol/0.15 mol % O₂/7.7 mol % toluene in CO₂ is available from the web pages of *Journal of Catalysis*

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Table 1:

Conversion of cinnamyl alcohol and selectivity to cinnamaldehyde measured during oxidation with molecular oxygen in supercritical carbon dioxide modified with different co-solvents and over different catalysts; in all cases the catalyst was pre-reduced in the same manner at 100°C and the catalytic data were recorded during the first day; (conditions: 150 bar, 80 °C, 0.15 mol % cinnamyl alcohol, 0.15 mol % O₂, 1.9 mol % co-solvent in CO₂).

Catalyst	Co-solvent	Conversion (%)	Selectivity (%)
0.5 wt % Ru/Al ₂ O ₃ (Engelhard 4871)	Toluene	- ^a	- ^a
0.5 wt % Pt/Al ₂ O ₃ (Engelhard 4751)	Toluene	- ^a	- ^a
0.5 wt % Pd/Al ₂ O ₃ (Engelhard 4586)	Toluene	60	71.5
0.5 wt % Pd/Al ₂ O ₃ (Engelhard 4586)	Acetone	44.3	62.8
0.5 wt % Pd/Al ₂ O ₃ (Engelhard 4586)	THF	33.3	64.3

^a below detection limit of GC

Table 2:

Catalytic activity results measured under different reaction conditions during cinnamyl alcohol oxidation over a palladium catalyst while *in situ* monitoring the structure of the solid catalyst by X-ray absorption spectroscopy; conditions: 0.4689 g of 0.5 wt % Pd/Al₂O₃ loaded in the EXAFS flow cell, T = 80 °C, 1.9 mol % toluene, 0.233 mol/min CO₂.

Pressure (bar)	Alcohol (mol %)	Oxygen (mol %)	Conversion (%)	Selectivity (%)	TOF (h ⁻¹)	Spectrum # ^a
120	0.15	-	5.2	62.6	172	- ^b
120	0.15	0.15	8.0	45.6	265	3
120	0.15	7.0	5.7	76.6	191	- ^b
150	0.15	0.15	2.7	81.7	91	4
150	0.15	7.0	7.0	87.3	234	5
150	-	5.0	-	-	-	6

^a EXAFS spectra shown in Figure 10

^b Not shown

Scheme 1

Reaction scheme of cinnamyl alcohol oxidation to cinnamaldehyde with molecular oxygen in supercritical CO₂ over an alumina-supported palladium catalyst.

Scheme 2

Reaction network observed during the oxidation of cinnamyl alcohol with molecular oxygen in supercritical CO₂ over a supported palladium catalyst. By-products detected only in traces are not included.

Figure captions

Figure 1 (colour on-line)

Dependence of cinnamyl alcohol conversion and selectivity to cinnamaldehyde on the concentration of toluene in the feed. The data were obtained over a stabilized (equilibrated) catalyst; conditions: 150 bar, 80 °C, $3.55 \cdot 10^{-4}$ mol/min cinnamyl alcohol, $3.55 \cdot 10^{-4}$ mol/min O₂, 0.233 mol/min CO₂, 2.5 g of 0.5 wt % Pd/Al₂O₃.

Figure 2 (colour on-line)

Conversion of cinnamyl alcohol and selectivity to cinnamaldehyde (a), and product/by-product distribution (b) as a function of pressure; conditions: T = 80 °C, 0.15 mol % alcohol, 0.15 mol % O₂, 1.9 mol % toluene in CO₂ (0.233 mol/min), 2.5 g of 0.5 wt % Pd/Al₂O₃.

Figure 3 (colour on-line)

Conversion of cinnamyl alcohol and selectivity to cinnamaldehyde (a), and product/by-product distribution (b) at 120 bar as a function of oxygen concentration in the feed; conditions: 120 bar, 80 °C, 0.15 mol % alcohol, 1.9 mol % toluene in CO₂ (0.233 mol/min), 2.5 g of 0.5 wt % Pd/Al₂O₃.

Figure 4 (colour on-line)

Conversion of cinnamyl alcohol and selectivity to cinnamaldehyde (a), and product/by-product distribution (b) at 150 bar as a function of oxygen concentration in the feed; conditions: 150 bar, 80 °C, 0.15 mol % alcohol, 1.9 mol % toluene in CO₂ (0.233 mol/min), 2.5 g of 0.5 wt % Pd/Al₂O₃.

Figure 5

Snapshots of the phase behaviour of the reaction mixture in dense carbon dioxide at 80 °C and containing 0.15 mol % cinnamyl alcohol, 0.15 mol % O₂, 7.7 mol % toluene at: (a) 126.4 bar in the biphasic region; (b) 128.7 bar in the intermediate region; (c) 130.6 bar in the single phase region; (a movie of the phase transition is provided in the electronic support information).

Figure 6 (colour on-line)

ATR-IR spectra recorded at the bottom of the view cell in the ν_2 -band region of CO₂ at increasing pressure for the 1.9 mol % toluene containing reaction mixture; the cinnamyl alcohol bands at 730 and 692 cm⁻¹ indicate the presence of an alcohol-rich liquid-like phase at 120 bar, a transition towards a single phase is observed at high pressure by the shift of the ν_2 -band of CO₂ from 660 to 662 cm⁻¹ and by the decrease of the alcohol bands; (conditions: 80 °C, 0.15 mol % cinnamyl alcohol, 0.15 mol % O₂, 1.9 mol % toluene in CO₂).

Figure 7 (colour on-line)

Comparison of the ATR-IR spectra recorded at the bottom of the view cell of a 0.15 mol % cinnamyl alcohol, 0.15 mol % O₂, 1.9 mol % toluene in CO₂ mixture at 120 bar and 80 °C in the region of the aromatic deformation bands (730 cm⁻¹ and 692 cm⁻¹) and of the ν_2 band of CO₂ (662 cm⁻¹) recorded with and without a catalyst layer of 0.5 wt % Pd/Al₂O₃ on the ZnSe crystal; in the catalyst pores supercritical-like conditions are reached at a lower pressure (see text).

Figure 8 (colour on-line)

On-line monitoring of the catalyst/fluid interface by ATR-IR spectroscopy during the selective oxidation of cinnamyl alcohol to cinnamaldehyde in the view cell equipped with IR-spectroscopy. On the right development of the carbonyl stretching band of cinnamaldehyde (1683 cm^{-1}) during reaction, on the left rise of by-products bands (3215 and 3134 cm^{-1}) at the end of the reaction; (conditions: 120 bar, $80\text{ }^{\circ}\text{C}$, 0.15 mol % cinnamyl alcohol, 0.15 mol % O_2 , 1.9 mol % toluene in CO_2 , 5 mg of 5 wt % $\text{Pd}/\text{Al}_2\text{O}_3$ deposited on the crystal).

Figure 9 (colour on-line)

Conversion as a function of time during selective oxidation of cinnamyl alcohol to cinnamaldehyde at 120 and 150 bar in the spectroscopic batch reactor view cell, extracted from the area of the carbonyl stretching band of cinnamaldehyde; conditions: $T = 80\text{ }^{\circ}\text{C}$, 0.15 mol % cinnamyl alcohol, 0.15 mol % O_2 , 1.9 mol % toluene in CO_2 , 5 mg of 5 wt % $\text{Pd}/\text{Al}_2\text{O}_3$ deposited on the crystal.

Figure 10 (colour on-line)

In situ EXAFS investigations on a 0.5 wt % $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst at the Pd K-edge under different reaction conditions: a) energy-calibrated and background-corrected XANES spectra; b) Fourier transformed EXAFS spectra; (1) in 5% H_2/He ; (2) in CO_2 at 120 bar; (3) in 0.15 % alcohol, 0.15 % O_2 , CO_2 at 120 bar; (4) in 0.15 % alcohol, 0.15 % O_2 , CO_2 at 150 bar; (5) in 0.15 % alcohol, 7 % O_2 , CO_2 at 150 bar; (6) in 5 % O_2 , CO_2 at 150 bar; (details in text).

Figure 11

Schematic representation of the phenomena taking place in the catalyst and at the Pd-particles; the presence of a dense liquid-like bulk phase, rich in aromatics, favours the dissolution of cinnamaldehyde; inside the pores mainly scCO_2 and cinnamaldehyde are present; the alcohol is not observed by ATR-IR spectroscopy due to a rapid dehydrogenation reaction.

Table 1

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^a below detection limit of GC

Table 2

Pressure (bar)	Alcohol (mol %)	Oxygen (mol %)	Conversion (%)	Selectivity (%)	TOF (h ⁻¹)	Spectrum # ^a
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120	0.15	7.0	5.7	76.6	191	- ^b
150	0.15	0.15	2.7	81.7	91	4
150	0.15	7.0	7.0	87.3	234	5
150	-	5.0	-	-	-	6

^a EXAFS spectra shown in Figure 10

^b Not shown

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11