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Palladium-Catalyzed Oxidation of Octyl Alcohols in “Supercritical” Carbon Dioxide

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Noble metal catalyzed aerobic oxidation of alcohols to carbonyl compounds or carboxylic acids is an efficient method, but the frequently observed catalyst deactivation and flammability of organic solvents in the case of water-insoluble alcohols limit the application range. We applied “supercritical” (dense) carbon dioxide as the solvent, a cheap and nonflammable medium with fair and tunable solubility in particular for weakly polar water-insoluble alcohols. The experiments were carried out in a continuous fixed bed reactor, over 0.5 wt% Pd/alumina, at 80–140°C and 75–125 bar. A comparative study of oxidation of 1- and 2-octanols to carbonyl compounds, chosen as model reactions, demonstrated that the method is well suited for the partial oxidation of secondary alcohols with molecular oxygen, whereas for primary alcohols the selectivity is low. In the oxidation of 2-octanol the selectivity was excellent (>99.5%) and independent of conversion. No significant catalyst deactivation was observed and the rate in CO_2 was higher by a factor of up to 2–4 compared to the rate of oxidation in nitrogen. The complex effects of pressure and oxygen concentration on the reaction rate have been interpreted by studying the phase behavior in a high-pressure view cell under reaction conditions. © 2001 Academic Press

Key Words: **octanol; oxidation; oxygen; Pd/alumina; over-oxidation; supercritical carbon dioxide; phase behavior; continuous fixed bed reactor.**

INTRODUCTION

The Pt-catalyzed oxidation of cinnamyl alcohol to cinnamaldehyde by oxygen was discovered by Strecker in 1855 (1). At present, supported noble metal catalysts in an aqueous medium are widely used for the oxidation of water-soluble alcohols and polyols (carbohydrates) in the synthesis of specialty and fine chemicals possessing carbonyl or carboxylic groups (2–6). The method is attractive from both economic and environmental points of view: molecular oxygen is a cheap and readily available oxidant and water is the co-product. Oxidations are typically performed with 5–10 wt% Pt or Pd supported on carbon or alumina, in the temperature range 40–90°C. Batch reaction time is usually 3–10 h. Catalyst deactivation is frequently observed and a relatively high catalyst/reactant mass ratio (0.2–0.5) is necessary even after promotion by lead or bismuth (5, 7).

Undesired formation of hydrogen by fast dehydrogenation of some alcohols and carbohydrates (3) is a major obstacle for safe operation. The explosion risk is even higher when flammable organic solvents (e.g., heptane (8)) are used for water-insoluble alcohols. Good knowledge of the reaction and strict control of the reaction conditions (oxygen concentration, temperature, and heat and mass transport) are necessary, even when working in a laboratory reactor.

An alternative solution may be to carry out the reaction in “supercritical” carbon dioxide ($scCO_2$; $T_c = 30.9°C$, $p_c = 73.8$ bar). Note that the term supercritical is generally used in chemistry for two- and multicomponent systems being beyond the critical parameters of the solvent or the mixture. In fluid theory, however, the expression is well defined only for single-component systems and has no meaning concerning the phase behavior of multicomponent systems since immiscibility phenomena can still occur beyond the mixture’s critical point (“retrograde condensation” (9, 10)). For convenience, the term “supercritical” is used here between quotation marks for the CO_2-containing dense phase at temperatures exceeding its mixture critical point (irrespective of further liquid phases present).

$scCO_2$ has several distinct advantages over conventional liquid solvents. Its solvent strength can be tuned by varying the density (pressure). This medium is especially suited for weakly polar, water-insoluble alcohols due to its low polarity. CO_2 is relatively inert, nonflammable, and has a comparatively high heat capacity—an important feature for exothermic reactions. “Supercritical” CO_2 is a fairly good solvent for many organic reactants and oxygen, and transport limitations typical for liquid solvents may completely vanish due to the high (gas-like) diffusivities. Products and solvents separate simply by releasing the pressure after reaction.

Supercritical solvents have found numerous applications in heterogeneous (11–13) and homogeneous catalysis (14, 15), but reports on partial oxidation in sc fluids are

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scarce. Oxidation of sc isobutane with air has gained importance because of the use of its oxidation products *tert*-butyl hydroperoxide and *tert*-butyl alcohol in the manufacture of propylene oxide and methyl *tert*-butyl ether, respectively (16–20). $scCO_2$ was used as the solvent in the conversion of toluene to benzaldehyde over CoO (21) and for the transformation of propylene to propylene glycol over copper iodide and copper oxide (22). Other interesting applications are the partial oxidation of cumene (23) and olefins (24), catalyzed by the steel reactor wall.

There are only a few examples of the partial oxidation of alcohols in $scCO_2$. In the oxidation of methanol over iron oxide based aerogels the temperature and catalyst loading were the crucial parameters governing the selectivities to formaldehyde, methyl formate, and dimethyl ether (25, 26). At temperatures above 200°C total oxidation dominated. Compared to conventional gas phase oxidation, application of $scCO_2$ provided a 3–5-fold increase in the rate of partial oxidation, and the onset of total oxidation shifted to higher temperatures. Ethanol oxidation over Pt/TiO_2 was carried out at 90 bar in the temperature range 150–300°C (27). Interestingly, the rate of partial oxidation to acetaldehyde was independent of O_2 concentration, though high O_2 concentration favored the consecutive reactions to CO and CO_2.

We have recently reported that $scCO_2$ is an excellent solvent for the partial oxidation of higher molecular weight, water-insoluble alcohols with oxygen (28). The aim of the present work is to get a deeper insight into the Pt-metal catalyzed oxidation reaction by combining the catalytic study with phase behavior measurements in a high-pressure view cell. The catalytic experiments have been carried out in a continuous fixed bed reactor. Partial oxidation of 1-octanol and 2-octanol have been chosen as model reactions, representing the transformation of water-insoluble primary and secondary alcohols. Octanols and octanals are major components of synthetic citrus oils in perfumery (29).

EXPERIMENTAL

Catalytic Tests

The reactions were performed isothermally in a tubular flow reactor with an inner diameter of 13 mm and 38-ml volume. The reactor setup has been published recently (30). Temperature was measured in the catalyst bed by a thermocouple well placed in the center of the bed. 1-Octanol and 2-octanol 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 high pressure and constant frequency. The constant pressure in the system was maintained by a pressure regulator with CO_2 or nitrogen. The total gas flow was controlled at the vent. Standard conditions for the parameter study were 95 bar and 120°C and the feed flow consisted of 5 mol% 2-octanol, 2.5 mol% oxygen, and 92.5 mol% carbon dioxide. This molar composition remained the same at all different pressures. Five grams of catalyst was used, corresponding to a catalyst bed length of 5 cm. The space time related quantity W/F was 1.02 g h mol^{-1} (W = weight of catalyst, F = molar feed rate). Glass beads (0.2-mm diameter, bed length of 5 cm) were filled above the catalyst bed. The catalyst was a 0.5% Pd/alumina (Engelhard No. 4586, cylindric tablets with 3.2-mm height and diameter; eggshell type, BET surface: 96 m^2 g^{-1}, metal dispersion: 0.29 determined by hydrogen chemisorption). The catalysts was reduced *in situ* in hydrogen at 100°C for 2 h prior to use, and its performance usually reached steady state within 2 h time on stream. Under the conditions applied in this study catalyst deactivation was minor. For the parameter study conversion was kept below 10% to minimize temperature gradients in the catalyst bed.

The liquid products were separated from CO_2 and analyzed by GC (HP-FFAP column) and identified by GC-MS. The selectivity and yield take into account all products formed.

Phase Behavior

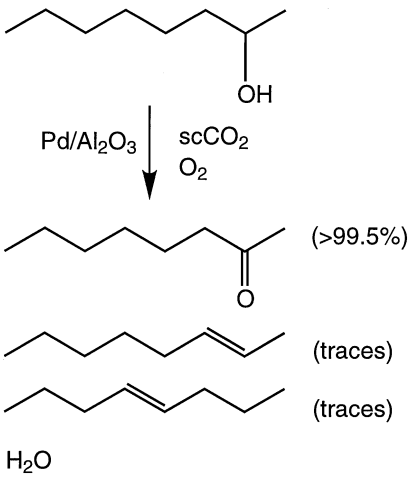
The phase behavior of the system under reaction conditions was investigated in a computer-controlled high-pressure view cell, equipped with on-line digital video imaging and recording. The magnetically stirred cell consisted of a horizontal cylinder equipped with a sapphire window covering the entire diameter and an opposite, horizontally moving piston equipped with another sapphire window for illumination of the system. This setup allowed the observation of even minor volumes of gaseous and liquid phases. The basic setup of the video imaging is described in detail elsewhere (31).

Due to limitations of the view cell in handling oxygen, the phase behavior experiments were carried out with a mixture of air and nitrogen instead of oxygen. Oxygen and nitrogen are similar in polarity and molecular mass, and the critical points of both gases (O_2: –119°C, 50 bar; N_2: –147°C, 34 bar) are far from that of CO_2 (31°C, 74 bar). We therefore assume that dilute mixtures of oxygen or nitrogen in CO_2 behave similarly. First, 5 mol% 2-octanol, 2.5 mol% of an O_2–N_2 mixture (30% air, 70% N_2), and 92.5 mol% carbon dioxide were supplied to the view cell. Changes in the phase behavior, induced by variation of temperature and pressure, were monitored.

RESULTS

Oxidation of 2-Octanol

Preliminary screening of various supported Pt, Ru, and Pd catalysts revealed that 0.5 wt% Pd/alumina afforded the best activity combined with good stability. Accordingly,



SCHEME 1. Products formed in the oxidation of 2-octanol.

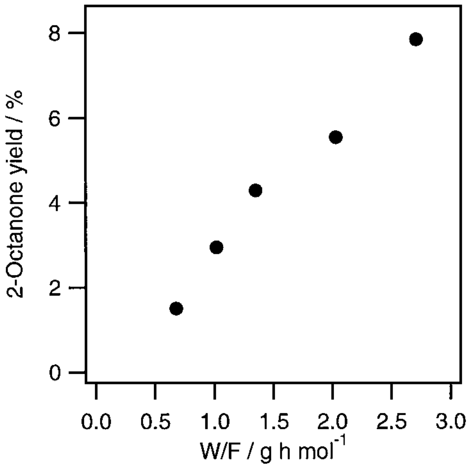


FIG. 2. Effect of space time related parameter W/F on the yield to 2-octanone. Conditions: 120°C, 95 bar, 5 g of 0.5% Pd/alumina, 5 mol% 2-octanol, 2.5 mol% O_2, 92.5 mol% CO_2.

all experiments discussed below were carried out with this catalyst.

Oxidation of 2-octanol yielded almost exclusively 2-octanone (Scheme 1). Even at high temperatures (140°C) and high conversion the side products 2-octene and 4-octene formed only in traces. Formation of olefins is attributed to dehydration of 2-octanol at the acidic sites of the alumina support and to subsequent isomerisation on Pd. No oxidative product degradation and acid formation were observed.

The 2-octanone yield went up exponentially by increasing the temperature (Fig. 1) and varied almost linearly with the space time related parameter W/F (Fig. 2).

The effect of pressure on the 2-octanone yield was rather complex and strongly depended on the set of other parameters (Fig. 3). Under standard conditions, at 120°C, the yield showed a maximum at around 100–110 bar (curve a). The maximum was less pronounced when the temperature was lowered to 100°C (curve b). When the reaction was carried out at 120°C with double the amount of oxygen in the feed, the yield rose monotonously with increasing pressure with only a weak "shoulder" at around 100 bar (curve c). The latter experiment was repeated at half space time ($W/F = 0.51$ g h mol^{-1}) and a similar linear dependence was found though the yields were lower.

Variation of oxygen concentration in the feed resulted in a bell-shaped curve of the 2-octanone yield, as shown in Fig. 4. The maximum at 7.5–10 mol% oxygen corresponds to a 200–300 mol% excess related to the stoichiometric ratio (octanol $+ \frac{1}{2}O_2$). Interestingly, at low oxygen concentration the ketone yield dropped to zero and the reaction did not proceed by anaerobic dehydrogenation at 120°C. It

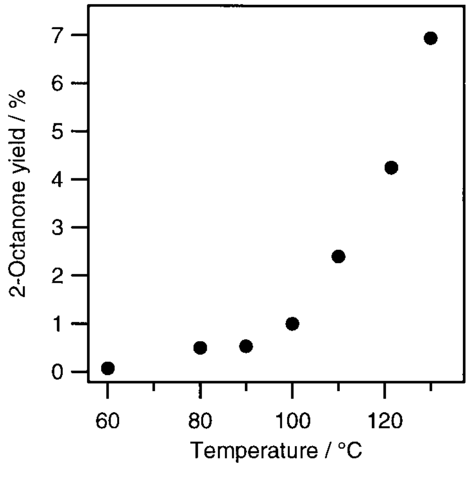


FIG. 1. Effect of temperature on the yield to 2-octanone. Conditions: 95 bar, 5 g of 0.5% Pd/alumina, $W/F = 1.02$ g h mol^{-1}, 5 mol% 2-octanol, 2.5 mol% O_2, 92.5 mol% CO_2.

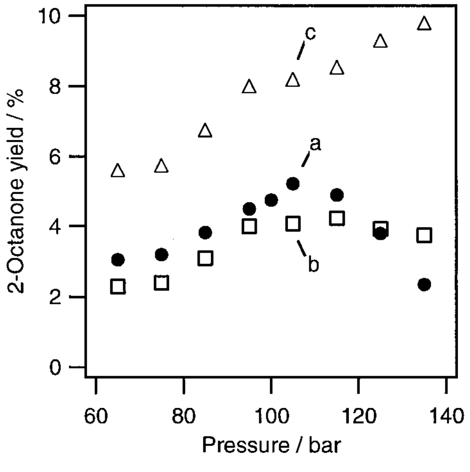


FIG. 3. Dependence of 2-octanone yield on the total pressure. (a) ● 120°C, $W/F = 1.02$ g h mol^{-1}, 2.5 mol% O_2; (b) □ 100°C, 2.03 g h mol^{-1}, 2.5 mol% O_2; (c) △ 120°C, 1.02 g h mol^{-1}, 5.0 mol% O_2. Other conditions: 5 g of 0.5% Pd/alumina, 5 mol% 2-octanol, rest CO_2.

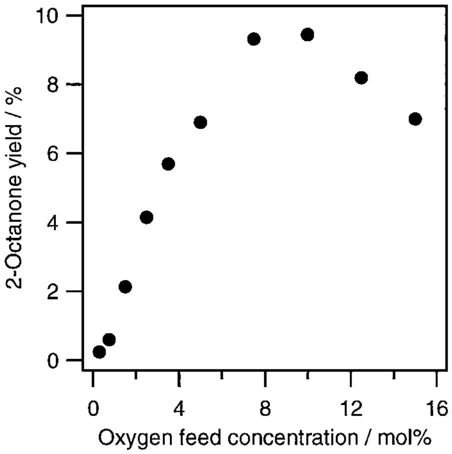


FIG. 4. Dependence of 2-octanone yield on oxygen concentration in the feed. Conditions: 120°C, 95 bar, 5 g of 0.5% Pd/alumina, W/F = 1.02 g h mol^{-1}, 5 mol% 2-octanol, rest O_2 and CO_2.

has been shown earlier that the best catalysts for anaerobic dehydrogenation of 2-octanol are Raney Ni (2) and copper chromite (32), and the necessary reaction temperatures are considerably higher (174 and 300°C, respectively).

When CO_2 was replaced by nitrogen, the 2-octanone yield dropped by a factor of 2–4. In nitrogen no optimum pressure was found and the yield increased steadily with increasing total pressure. Some examples are listed in Table 1 to illustrate the solvent effect of dense CO_2.

Variation of the reaction parameters revealed that the 2-octanone yield could be increased without any loss in selectivity. For example, 46% yield was obtained at 140°C by applying a relatively high space time (W/F) (Table 2). However, under these conditions there was a significant temperature gradient (10°C) in the catalyst bed. The only limit to further increasing the yield of the strongly exothermic reaction was the insufficient rate of heat transport in the reactor setup used.

Oxidation of 1-Octanol

Oxidation of 1-octanol resulted in a mixture of 1-octanal, octanoic acid, and octyl octanoate as major products (Scheme 2). Traces of octyl ether were also found among the products. A parameter study revealed that reasonably good octanal selectivity can be achieved only at low conversions (Table 3). The influence of reaction conditions on the rate and octanal selectivity is illustrated by two typical examples in Figs. 5 and 6. Increasing the temperature from 80 to 140°C reduced the octanal selectivity to about one-half, though the 1-octanol conversion was only 12% at 140°C (Fig. 5). Above 120°C the major product was the acid, not the aldehyde. Similar, but less pronounced, effects on the conversion rate and selectivity were observed when the space time or the oxygen concentration in the feed were increased (not shown here). The only exception was the variation of the total pressure in the system (Fig. 6). Though the alcohol conversion increased with increasing pressure, the aldehyde selectivity slightly increased.

TABLE 1

Oxidation of 2-Octanol in Nitrogen or Carbon Dioxide

Solvent (diluent)	p (bar)	T (°C)	W/F (g h mol^{-1})	Conv. (%)
Nitrogen	85	100	2.03	1.5
Carbon dioxide	85	100	2.03	3.1
Nitrogen	95	120	1.02	1.2
Carbon dioxide	95	120	1.02	4.3

Note. Conditions: 5 g of 0.5 wt% Pd/alumina, 5 mol% 2-octanol, 2.5 mol% O_2, 92.5 mol% CO_2.

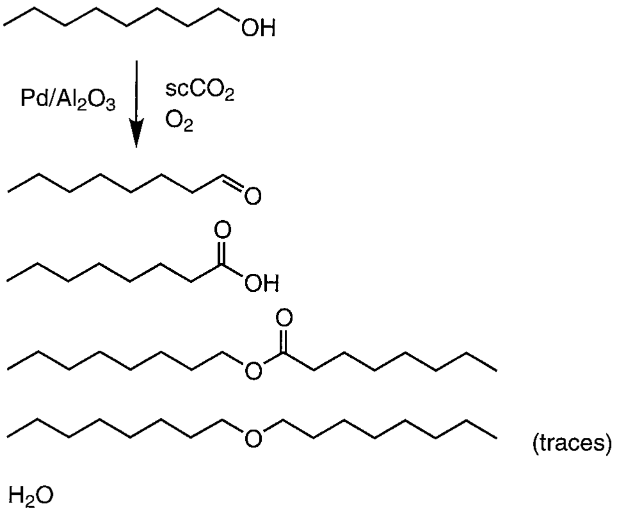
TABLE 2

Some Examples of the Oxidation of 2-Octanol at Higher Conversion

2-Octanol (mol%)	Oxygen (mol%)	p (bar)	T (°C)	W/F (g h mol^{-1})	Conv. (%)	Sel. (%)
6	3	110	140	2.71	46	>99.5
6	3	110	140	1.02	21	>99.5
10	2.5	95	120	1.01	11.6	>99.5

Note. Conditions: 5 g of 0.5 wt% Pd/alumina, solvent $scCO_2$.

It seems that in this reaction the selectivity to the aldehyde intermediate is primarily determined by the alcohol conversion. This correlation is illustrated in Fig. 7 by all data obtained in a broad range of reaction conditions. The dashed hyperbolic curve reflects the limited potential of the catalyst (Pd/alumina) and solvent ($scCO_2$) for the partial oxidation of 1-octanol.



SCHEME 2. Products formed in the oxidation of 1-octanol.

TABLE 3

Oxidation of 1-octanol to Octanal

T (°C)	W/F (g h mol^{-1})	Conv. (%)	Sel. (%)
80	1.02	3.3	73
140	1.02	10.5	38
140	2.71	22.0	27

Note. Conditions: 5 g of 0.5 wt% Pd/alumina, 3 mol% 1-octanol, 6 mol% O_2, 91 mol% CO_2, 110 bar.

Phase Behavior

The phase behavior of the system under reaction conditions was investigated in a magnetically stirred high-pressure view cell. Measurements were carried out along the bubble-point phase boundary of the gas–liquid equilibrium in the temperature region of the catalytic experiments. Figure 8 shows typical interlaced video images in the view cell under reaction conditions: a small alcohol-rich liquid phase at the bottom of the reactor is topped by a CO_2-rich “supercritical” phase.

The results of the phase behavior experiments are shown in Fig. 9. The phase behavior of the reaction system under conditions of the oxidation reaction was found to be parallel to that of the octanol–CO_2 system (33). This binary mixture shows type II behavior (10), according to the classification of Scott and van Konynenburg (34). That is, the liquid–liquid immiscibility is limited to low temperatures, not interfering with the gas–liquid critical line of the mixture. The addition of the 2.5 mol% nitrogen–oxygen mixture to the octanol–CO_2 system resulted in a shift of the gas–liquid phase boundary to higher pressures by about 20 bar.

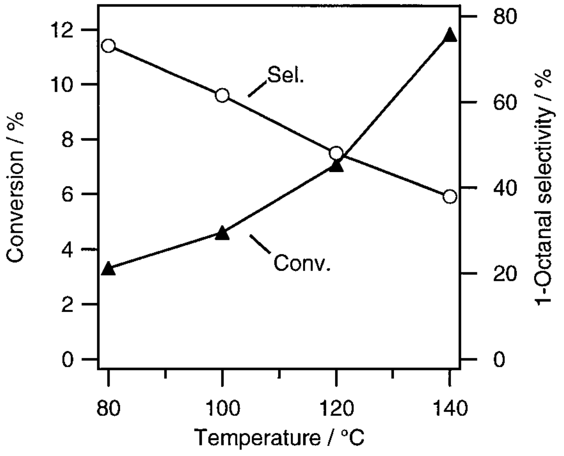


FIG. 5. Influence of temperature on 1-octanol conversion and 1-octanal selectivity. Conditions: 110 bar, 6 mol% O_2, 3 mol% 1-octanol, 91 mol% CO_2, 5 g of 0.5% Pd/alumina, W/F = 1.02 g h mol^{-1}.

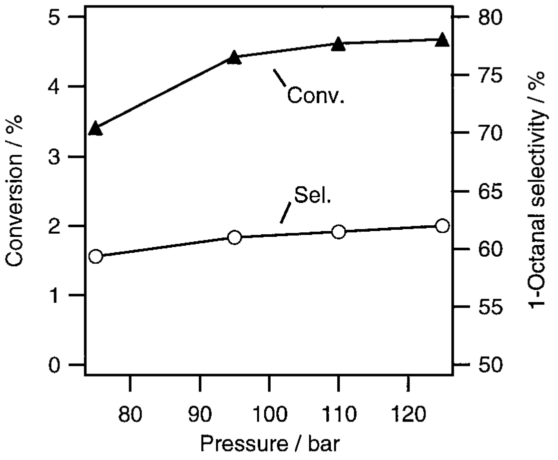


FIG. 6. Dependence of 1-octanol conversion and 1-octanal selectivity on the total pressure. Conditions: 100°C, 6 mol% O_2, 3 mol% 1-octanol, 91 mol% CO_2, 5 g of 0.5% Pd/alumina, W/F = 1.02 g h mol^{-1}.

DISCUSSION

Oxidation of Alcohols in $scCO_2$—Scope and Limitation

The model studies with 1- and 2-octanol demonstrate that the Pd-catalyzed aerobic oxidation in $scCO_2$ is limited to the transformation of secondary alcohols to ketones. This type of reaction is fast and highly selective. For example, 46% 2-octanone yield was obtained at only 40-s residence time and the selectivity was almost 100% (Table 2). No catalyst deactivation or metal leaching was observed over a time-on-stream period of 110 h. Optimization of the reaction conditions and catalyst has not been attempted, yet still, the studies indicate that the selectivity to ketone is very high and independent of alcohol conversion. A comparison with the literature data in Table 4 indicates that the selectivity in $scCO_2$ is outstanding. Unfortunately, no fair

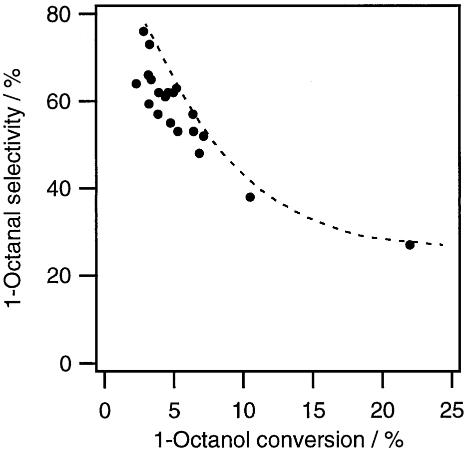


FIG. 7. Dependence of 1-octanal selectivity on 1-octanol conversion. Conditions: 80–140°C, 75–125 bar, 5 g of 0.5% Pd/alumina, W/F = 0.68–2.71 g h mol^{-1}, 3–10 mol% 1-octanol, 1.5–10 mol% O_2, rest CO_2.

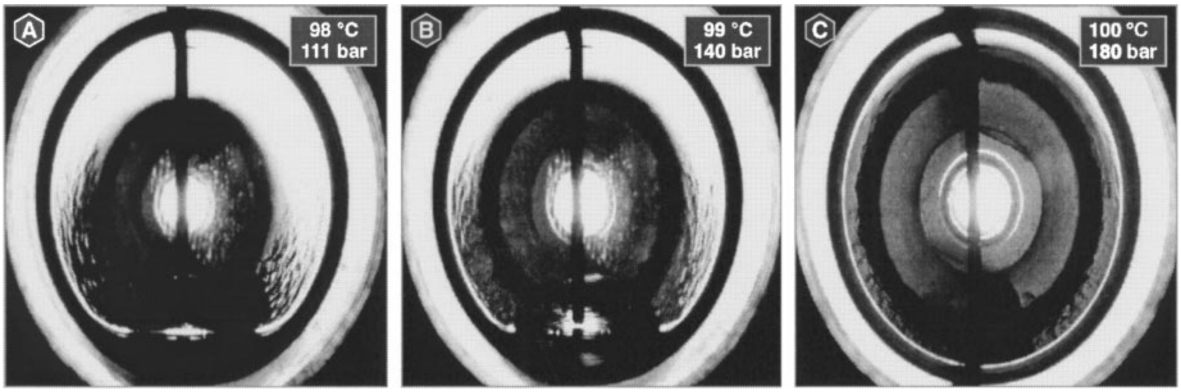


FIG. 8. Interlaced video images of the view cell under reaction conditions (5 mol% 2-octanol, 2.5 mol% O_2–N_2 mixture, 92.5 mol% CO_2), showing a two-phase equilibrium of a liquid 2-octanol-rich phase and a "sc" CO_2-rich phase at 100°C. The amount of liquid phase decreases with increasing pressure. The vertical line is the thermocouple and at the bottom of the reactor the liquid phase is clearly visible. The round bright spot at the opposite end of the cell is the sapphire window used for illumination. In the middle of the reactor at the bottom lies the magnetic stirrer.

comparison of the reaction rates is possible due to the strikingly different reaction conditions applied (temperature, reactor operation mode). On the basis of the comparative experiments in nitrogen and CO_2 (Table 1), we can conclude that dense CO_2 has a remarkable positive solvent effect on the oxidation rate.

Aerobic oxidation of primary alcohols to aldehydes in $scCO_2$ is nonselective. At low conversion the aldehyde is the major product, but with increasing conversion the corresponding acid and ester (formed from the reactant and product) become the dominant products (Figs. 5 and 7; Table 3). Interestingly, similar behavior was observed in the Pt-catalyzed aerobic oxidation of 1-dodecanol in water (4, 7). The initial high selectivity to aldehyde was diminished with increasing conversion due to rapid hydration of the aldehyde, followed by dehydrogenation of the geminal diol to the corresponding carboxylic acid. The similar selectivity patterns obtained in the oxidation of primary aliphatic alcohols in water and in $scCO_2$ indicate that—at least in this respect—the solvent has no significant influence on the reactions occurring on the metal surface. Apparently, the presence of co-product water on the metal surface is sufficient for the rapid hydration of aldehyde intermediate, as shown in Scheme 3. Water is regenerated after dehydrogenation to acid, and ester formation with the reactant alcohol increases further the amount of water on the catalyst surface available for hydration. Note that deactivated carbonyl compounds, e.g., aromatic aldehydes and particularly ketones, hydrate only to a negligible extent.

Table 4 lists the characteristic features of various heterogeneous octanol oxidations with oxygen reported in the

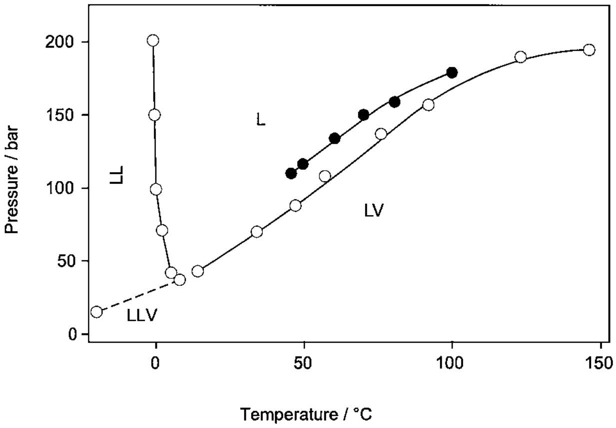
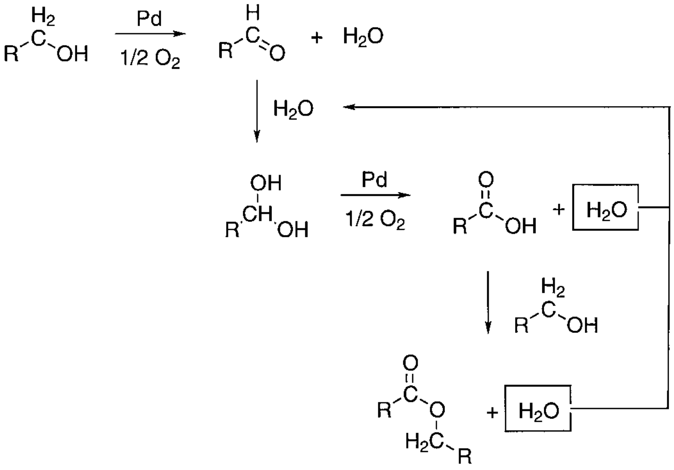


FIG. 9. Isoplethic bubble-point gas–liquid phase boundary of the ternary mixture CO_2/2-octanol/air (●) compared with the isoplethic phase boundaries of the CO_2/2-octanol binary mixture (○) (6.3 mol% 2-octanol in CO_2, data taken from Ref. (33)). L: one liquid region; LL: two partially miscible liquid phases; LV: liquid–vapor coexistence region; LLV: line of coexistence of two partially miscible liquid phases with a common vapor phase. Note that the region of liquid–vapor coexistence is limited by the dewpoint gas–liquid phase boundary at low pressures (not drawn).



SCHEME 3. Formation of acid and ester byproducts during oxidation of 1-octanol.

TABLE 4

Oxidation of Octyl Alcohols to Carbonyl Compounds (1-Octanal, 2- and 3-Octanone) at Atmospheric Pressure

Alcohol	Oxidant	T (°C)	Catalyst	Solvent	Operation	Reaction time(h)	Yield (%)	Sel. (%)	Ref.
1-Octanol	Air	340	Au	—	Continuous	—	83	92	(35)
1-Octanol	No[a]	265–300	Cu/MgO	—	Continuous	—	58	99	(36)
1-Octanol	Oxygen	20	Pt	Ethyl acetate	Batch	20	21	—	(37)
1-Octanol	No[a]	250–300	CuO	—	Continuous	—	98	—	(38)
1-Octanol	No[a]	450	Cu–Zn–Bi	—	Continuous	—	94	95	(39)
2-Octanol	No[a]	300–325	Cu chromite	No solvent	Batch	3.8	37	—	(32)
2-Octanol	Oxygen	20	Pt	*n*-heptane	Batch	96	80	92	(8)
2-Octanol	Oxygen	60	Ru–Co–hydrotalcite	Toluene	Batch	2	97	97	(40)
3-Octanol	No[a]	174	Raney Ni	No solvent	Batch	15	83	92	(2)

[a] Dehydrogenation without oxidant.

literature. The data show that the highest yields (up to 98%) to 1-octanal could be achieved by copper-catalyzed anaerobic dehydrogenation at elevated temperatures (38). Under these conditions water is absent and further oxidation is minor.

Oxidation of 2-Octanol—Role of Phase Composition and Over-Oxidation of Pd

For the interpretation of the rate of 2-octanol oxidation, two important points have to be discussed: the role of density and phase composition of the reaction mixture and the effect of surface oxygen concentration.

The phase behavior studies have revealed that the reaction mixture consists of two phases over the whole temperature and pressure range investigated: a 2-octanol-rich liquid phase and a CO_2-rich “supercritical” phase. Changes in the composition of these phases can be interpreted as follows:

(i) The solubility of 2-octanol in CO_2 depends on the density of the mixture (41). Because at standard reaction conditions (120°C and 95 bar) the density of CO_2 (0.16 g ml^{-1}) is 3 times lower than the critical density of CO_2 (0.47 g ml^{-1}), the alcohol solubility is relatively low, which explains the presence of a 2-octanol-rich liquid phase in the whole range of conditions applied. Parallel to the effect of temperature and pressure on the density of the CO_2-rich phase, the solubility of 2-octanol increases with increasing total pressure and decreasing temperature. Isobaric addition of oxygen results in a decrease of density of the CO_2-rich phase and thus diminishes the solubility of 2-octanol.

(ii) The solubility of oxygen in the octanol-rich phase increases with increasing total pressure and oxygen partial pressure and with decreasing temperature.

The phase behavior of the ternary system containing oxygen (nitrogen) shows a similar characteristic along the isoplethic gas/liquid bubble-point phase boundary compared to that of the binary system 2-octanol/CO_2. Addition of oxygen (and nitrogen) results in a shift of the mentioned line to higher pressures. The change of composition of the two phases influences the reaction. Increasing oxygen concentration in the liquid phase leads to higher surface oxygen coverage and thus higher rates (yields). These effects can be clearly observed when increasing the total pressure (Fig. 3) or the oxygen feed concentration at constant pressure (Fig. 4), but only at low values up to the maxima. The combination of these two effects indicates that it is the liquid phase that is in contact with the catalyst and controls the reaction over the metal surface.

The decline of 2-octanone yield at high oxygen concentrations in the feed (Fig. 4) is attributed mainly to “over-oxidation” of the metal surface. Over-oxidation is a thoroughly investigated phenomenon in the aerobic oxidation of alcohols over platinum metal catalysts (3, 42–44). The basis of this unusual behavior is that the activity of the reduced metal for alcohol oxidation is remarkably higher than that of the oxygen-covered surface. Though oxygen is necessary for the reaction, too high oxygen coverage leads to a drop in the number of reduced surface metal sites available for alcohol adsorption and oxidation and thus lowers the reaction rate. The correlation presented in Fig. 4 may formally be described by the following rate equation, where Θ_i represent corresponding surface coverages (4):

$$r = k \cdot (\Theta_{\text{oxygen}})^m \cdot (\Theta_{\text{alcohol}})^n. \quad [1]$$

Note that changing only one parameter at a time (pressure or oxygen concentration) still does not allow a clear separation of the effects of phase composition and surface oxygen concentration due to the mutual dependence of the parameters varied. Increasing the total pressure at constant oxygen feed concentration enhances oxygen solubility in the alcohol-rich phase, which is in contact with the catalyst surface, and this change can also lead to too high surface oxygen coverage and thus over-oxidation (Fig. 3). The strikingly different effects of increasing total pressure on the octanone yield when the set of other parameters was varied are also attributed to strong interactions between the parameters, i.e., their complex influence on the density and solubilizing power of the liquid phase, and on the oxygen coverage on Pd.

CONCLUSIONS

Partial oxidation of secondary alcohols to ketones in "supercritical" CO_2 with molecular oxygen has distinct advantages compared to conventional processes. The selectivity of the reaction in dense CO_2 is outstanding, and the rate of conversion is remarkably higher than that of vapor phase oxidation under similar conditions, in the presence of a nitrogen diluent. Besides the higher rate, the absence of any significant catalyst deactivation is also attributed to the presence of "supercritical" CO_2 as solvent. Furthermore, application of the nonflammable CO_2 is safer and provides easier product separation compared to liquid phase oxidations in organic solvents.

Our study also demonstrates that interpretation of the catalytic performance in dense ("supercritical") CO_2 requires a careful analysis of the phase behavior of the system under reaction conditions, a matter that is often ignored in the pertinent literature.

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