Noble metal catalysed aerial oxidation of alcohols to aldehydes in supercritical carbon dioxide

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Platinum and palladium supported on carbons are shown to be excellent catalysts for selective oxidation of organic alcohols to aldehydes ($>99\%$) at high yields using dioxygen as an oxidant in supercritical CO_2 fluid medium. There is no detectable over-oxidation of the product to acid and no metal leaching that are commonly encountered in the conventional aqueous medium. It is also found that the hydrophobicity/hydrophilicity of the catalyst surface relative to the CO_2 solvent plays a crucial role in the resulting catalytic activity and stability. Adding 1% Teflon onto the noble metal–carbon catalysts dramatically enhances the activity and lifetime of the catalysts during the aerial oxidation of fine chemicals in $scCO_2$ fluid.

KEY WORDS: supercritical carbon; oxidation; catalysis; hydrophobic surface

1. Introduction

One of the biggest challenges in fine chemical oxidation catalysis is to use molecular oxygen as an efficient and selective oxidant to provide useful products and intermediates [1]. If successful, they could replace the currently favoured stoichiometric oxidants (manganates, chromates, etc.) which generate significant waste. One approach is to use noble metals that have the ability to activate molecular oxygen for the selective oxidation of organic molecules in the liquid phase below 50 °C [2]. However, there are currently unresolved solvent problems prohibiting industrial applications. Organic solvents used for this reaction are unacceptable to industry due to the risk of forming organic peroxides. Water is therefore the proposed solvent of choice for water-soluble substrates [3]. A water-detergent system has been proposed to widen the application to water-insoluble reactants [3]. Unfortunately, there are severe problems of product selectivity, catalyst deactivation and metal leaching when the reaction is in water [4].

Supercritical carbon dioxide ($scCO_2$) has recently emerged as an attractive solvent for chemical reactions because it is non-toxic [5], non-flammable, inexpensive and environmentally benign. In addition, $scCO_2$ can display tuneable solvent properties depending on the temperatures and pressures used. Very recently, $scCO_2$ has begun to create an impact on catalytic reactions, such as hydrogenation of olefins [6,7], hydroformylation [8], carbon–carbon bond formation [9] and Friedel–Crafts alkylation [10]. The unsatisfactory solvent property of noble metal catalysed oxidation reactions in both organic solvents and water has led to the search for alternatives. We are particularly interested to investigate whether there are any unique and real advantages of using supercritical CO_2 as a solvent for this system.

In this communication letter we demonstrate, that an extremely good selectivity to aldehydes ($>99\%$), at high yields can be achieved through the oxidation of a range of benzyl alcohols by molecular oxygen using carbon-supported noble metal catalysts in $scCO_2$. A lower selectivity to aldehydes is obtained over the same catalysts in aqueous solution due to the uncontrolled over-oxidation of alcohols to acids. Thus, the work suggests that the use of $scCO_2$ as a solvent creates new opportunities in noble metal catalysed selective oxidation reactions. A preliminary account of this work was reported in the 220th ACS National meeting at Washington, DC [11]. It is also interesting to note that an independent study of aerial oxidation of benzyl alcohols over noble metals in $scCO_2$ by Baiker and co-workers drawing a similar conclusion has recently appeared [12].

2. Experimental

All experiments were carried out in a stainless-steel 100 cm^3 Parr autoclave. A series of carbon-supported platinum and palladium catalysts were used (100 mg, 5 wt% metal loading) and alcohol (0.29 mmol) was added into the autoclave. O_2 (5 bar partial pressure) and then liquid CO_2 were pumped into the autoclave using a booster pump to give the desired pressure. The reaction was stirred at the set temperature for the desired reaction time (24 h). Stirring was achieved by means of an overhead magnetic stirrer, the motor was set at $1/2$ maximum speed, giving approximately 360 rpm. After the reaction, the autoclave was allowed to cool to room temperature. The autoclave was vented into a suitable solvent (50 cm^3), opened once atmospheric pressure was reached and extracted with a further quantity of solvent

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(50 cm^3). The samples were analysed quantitatively using LC-MS, GC-MS and/or UV.

We modified a published method for the preparation of a noble metal catalyst on hydrophobic carbons [13]. Typically, the commercial Pt/graphite catalyst was dispersed in hot demineralised water (30 cm^3 using an ultrasound bath). The resulting suspension was heated to 60 °C with stirring before adding the appropriate amount of Teflon solution (Teflon solution purchased from BDH). Upon cooling and/or addition of acid the mixture flocked. The precipitated solid was filtered gently using a fine filter paper – grade 50. The catalyst was dried overnight at 105 °C before calcination in air for 15 min at 350 °C so that the deposited Teflon covered the carbon surface. It is noted that the melting temperature for Teflon is ca. 316 °C.

3. Results

3.1. Choice of substrate

Our initial experiments were performed using a range of commercially available metal catalysts supported on various carbons-based supports. In order to evaluate the conditions such that oxidation is definitely taking place in $scCO_2$ solvent, a *bulk* alcohol substrate, 9-anthracene methanol, was chosen. Starting material was mixed with a solid-carbon-supported noble metal catalyst and then charged with O_2 and CO_2 in a stirred autoclave. Since the alcohol exists as a solid (mp = 162–164 °C) at the reaction temperature (65 °C), hence, its low vapor pressure at the temperature and the hanging basket containing catalyst particles in the reactor reduces the extent of a direct vapor-phase or liquid-phase reactions with the solid catalyst. Control experiments using N_2/O_2 mixture instead of CO_2/O_2 at identical ratios and pressures were also conducted such that the extent of the vapor-phase reaction could be measured. Our results presented in figure 1 clearly showed that noble metal Pt catalysed oxidation of this substituted benzyl alcohol could be successfully conducted in $scCO_2$ to give the corresponding aldehyde as the sole product. Pd is also found to be effective for the reactions in $scCO_2$, as shown in figure 2, and represented in scheme 1.

3.2. Pressure considerations

Figure 1 demonstrates that the oxidation of 9-anthracene methanol over Pt catalysts increases rapidly with increasing CO_2 pressure. The two curves are well above the curve displayed by N_2. The solubility of organic compound in $scCO_2$ is dependent on the density of the $scCO_2$ fluid, which in turn depends on applied pressures [14]. This accounts for the fact that the conversion depends on the applied pressure as seen in figure 1. Significantly higher conversions can be achieved at corresponding pressures when the same Pt/graphite catalyst is modified with 1% Teflon. It is noted that the modification of Pt/graphite with Teflon renders the catalyst strongly hydrophobic.

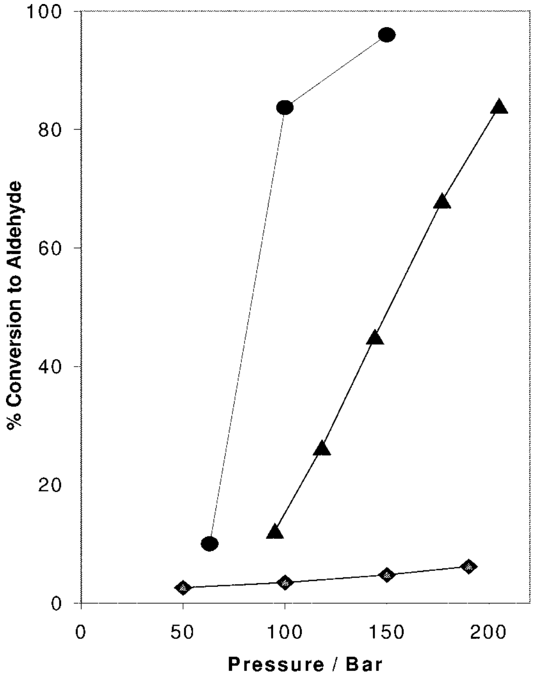
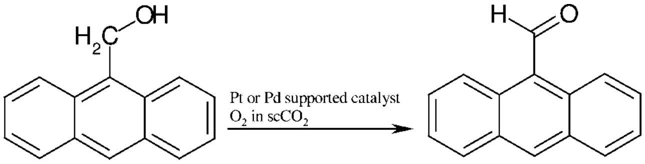


Figure 1. Pressure vs. conversion plots for the oxidation of 9-anthracene methanol catalysed by (●) Pt/graphite, CO_2/O_2; (▲) 1% Teflon Pt/graphite, CO_2/O_2; and (◆) Pt/graphite, N_2/O_2.



Scheme 1.

Figure 2 shows that the unmodified 5% Pd on high surface area charcoal ((Δ) symbol) showed consistently higher activities than the control N_2 experiments; these values are much poorer in comparison to the 5% Pt/graphite at the same corresponding pressures. From figure 2 it can be seen that for applied pressures higher than 100 bar over the unmodified 5% Pd charcoal catalyst the alcohol conversions either level off or even slightly decrease. The curve profiles, in particular at the high pressure regime, can be altered depending on whether the samples are wet, freshly dried from oven (120 °C overnight), pre-mixed with 20 mg of 5 Å molecular sieves or a combination of these treatments. We attribute the poor catalytic performances at high CO_2 pressures to a kind of pressure dependent poisoning effect. It is known that oxidation of alcohols will produce water as a main *by-product* and the charcoal surface containing polar groups such as phenolic and carboxylic groups [15] will doubtless stabilise the water film against evaporation on the catalyst surface. It is therefore conceivable that significant amounts of liquid water when produced at elevated pressure could act as a poison to deactivate the highly porous Pd/carbon catalyst through pore blockage or creating a passive liquid layer. In contrast, $scCO_2$ is able to carry considerably quantities of moisture in the fluid CO_2 phase if the water is all released to

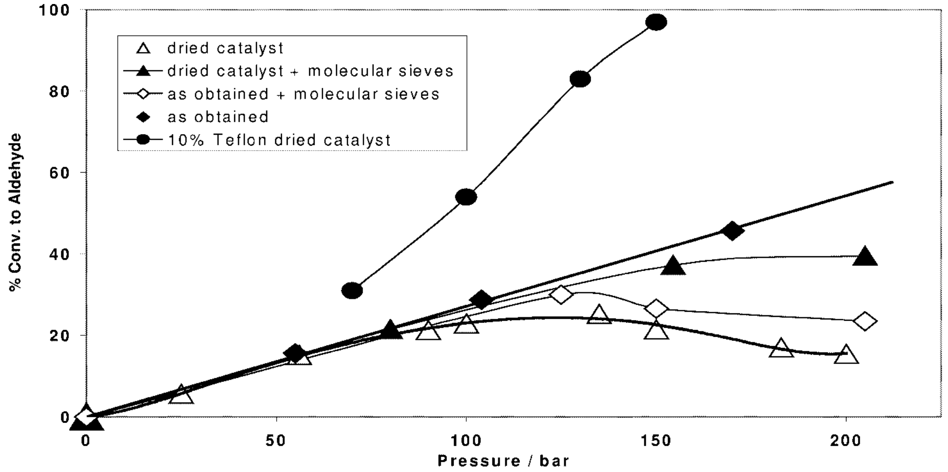


Figure 2. The effect of water and 10% Teflon on 5% palladium/charcoal catalysts.

Table 1
Catalytic oxidation of benzyl alcohols and related compounds over carbon-supported noble metals in $scCO_2$.

Catalyst	SA ($m^2\ g^{-1}$)	Substrate	T (°C)	P_{O_2} (bar)	Medium (bar)	Conversion (%)	RCHO sel. (%)	RCOOH sel. (%)
Pt/C[a]/1% Teflon	75	9-anthracene methanol	65	5	CO_2 (150)	96	>99	n.o.
Pt/C[a]	121	9-anthracene methanol	65	5	H_2O (liquid)[c]	100	~65	~35
Pt/C[a]	121	9-anthracene methanol	65	5	CO_2 (144)	45	>99	n.o.
Pd/C[b]	805	9-anthracene methanol	65	5	CO_2 (150)	22	>99	n.o.
Pd/C[b]/1% Teflon	687	9-anthracene methanol	65	5	CO_2 (150)	97	>99	n.o.
Pd/C[b]	805	Benzyl alcohol	60	5	CO_2 (150)	63	>99	n.o.
Pd/C[b]	805	3-phenoxybenzyl alcohol	60	5	CO_2 (150)	72	>99	n.o.
Pd/C[b]	805	Dihydro-cholesterol	60	5	CO_2 (180)	40	>99	n.o.
Pt/C[a]/1% Teflon	805	*n*-decanol	60	5	CO_2 (110)	92	92.2	n.o.
Pt/C[a]/1% Teflon	75	*m*-hydrobenzoin	80	0.2	CO_2 (150)	78.8	21.6% benzoin 43.9% benzil 26.1% benzaldehyde	n.o.
Pd/C[b]	805	Diphenylmethane	100	5	CO_2 (150)	17	>99 (Ph_2CO)	n.o.

[a] A commercial Johnson Matthey catalyst (5% metal loading), graphite support.
[b] A commercial Johnson Matthey catalyst (5% metal loading), charcoal support.
[c] 60 mg substrate dissolved in 5 cm^3 THF; 400 μl Triton X-114 used as a surfactant in 100 cm^3 DI water; n.o. – not observed.

the fluid phase leading to a high conversion of alcohols [16] (much higher than water produced from the reaction). Thus the key research is to develop a hydrophobic catalyst surface. Hence, the water molecule when produced can be repelled from the solid catalyst surface into the $scCO_2$ fluid phase. Figures 1 and 2, and table 1 show clearly the effectiveness of adding the hydrophobic Teflon to the Pt/graphite and Pd/charcoal catalysts in enhancing their catalytic activity.

3.3. Concentration and pressure of oxygen (mole ratios)

The initial experiments were carried out using a large excess of oxygen (5–10 bar). However, re-testing of the catalyst indicates high levels of oxygen can poison the catalyst (table 2). A similar catalyst deactivation due to the high level of oxygen “over-oxidising” the metal surface has been reported [17]. Later experiments were therefore carried out using diluted oxygen in CO_2 (0.04 bar, 0.26 mmol O_2). The adoption of equivalent molar quantities of gaseous oxygen allows the catalyst to be reused without serious loss of activity.

3.4. Different substrates

Table 1 shows that the noble metal catalysed oxidations of 9-anthracene methanol, benzyl alcohol, 3-phenoxybenzyl alcohol and diphenylmethane (hydrocarbon) in $scCO_2$ all re-

Table 2
Alcohol conversions using different oxygen concentrations over 1% Teflon 5% Pt/graphite catalyst.

Substrate	T (°C)	P_{O_2} (bar)	P_{CO_2} (bar)	Conversion (%)
9-anthracene methanol[a]	65	5	100	81
9-anthracene methanol[b]	65	5	100	Trace
9-anthracene methanol[a]	65	0.2	100	82
9-anthracene methanol[b]	65	0.2	100	62
9-anthracene methanol[a]	65	0.04	100	80
9-anthracene methanol[b]	65	0.04	100	81
Benzyl alcohol[a]	60	10	150	63
Benzyl alcohol[a]	60	5	150	63

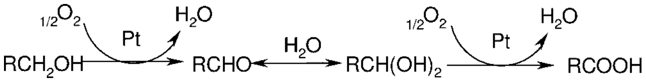
[a] First test.
[b] Second test (atomic absorption technique revealed that the metal loading remained virtually unchanged).

sulted in extremely high selectivity to the corresponding carbonyl compounds (>99%), at high yields and with no noticeable acid formation. We chose oxidation of 9-anthracene methanol in aqueous solution over the same unmodified Pt/C catalyst as a comparison to the $scCO_2$ medium. When the oxidation is operated in water, the 9-anthraldehyde selectivity (∼65%) is significantly lower, at the expense of 9-anthracenecarboxylic acid production. It is interesting to find that higher conversions of 9-anthracene methanol at corresponding pressures are obtained in $scCO_2$ when noble metals are supported on increasingly hydrophobic carbon surfaces (Teflon-modified carbon > graphite > charcoal) instead of the same order as their increasing surface areas. It is noted that the noble metal catalysts can effectively oxidise other alcohols (benzyl alcohol to benzaldehyde; 3-phenoxybenzyl alcohol to 3-phenoxybenzaldehyde; dihydro-cholesterol to dihydro-cholesterone; *n*-decanol to *n*-decanal) and related organic molecules (diphenyl methane to diphenylformaldehyde) with high selectivity to carbonyl products in $scCO_2$ using gaseous oxygen as the oxidant. It should be noted that high selectivity to the corresponding aldehyde (>92%) can still be achieved when *n*-decanol is oxidised by oxygen in $scCO_2$ over the 1% Teflon Pt/graphite catalyst. In this case, no extra stabilisation due to the electron delocalisation off the benzene ring as shown in the cases of benzyl compounds is expected. It is also interesting to find that the oxidation of *m*-hydrobenzoin (diol) in $scCO_2$ over the noble catalyst facilitates carbon–carbon cleavage of the molecule leading to various carbonyl products such as benzil (diketone), benzoin (monoketone) and benzaldehyde but again no acid product was detected under the conditions.

4. Discussion

As stated in the introduction there is an increasing demand to use molecular oxygen from air as an oxidant for industrial oxidation processes with regards to the process economy and environmental impacts.

Noble metal catalysts are thus interesting candidates that can activate dioxygen for oxidation reactions in both organic and aqueous media [2]. There has been reported a considerable amount of work over the past years in the investigation of noble metal catalyst for aerial oxidation of fine chemical in water medium. However, observations from this work and others in the literature show that a number of kinetic problems prevail when the same reactions are carried out in the aqueous phase [2]. These include strong adsorption of non-polar by-products or intermediates [18], leading to a poor rate of oxidation, and acids produced from the over-oxidation, leading to a serious corrosion [4] and surface restructuring [19,20]. There is also a rapid deactivation due to the presence of gaseous oxygen even for a low concentration of oxygen. Hence, controlled introduction of gaseous oxygen (stepwise) for the oxidation reaction is essential [17]. Such problems are not generally observed in many gas phase catalysed oxidation (combustion) reactions over noble metal catalysts, so these problems seems to be characteristic of aqueous phase oxidation. Notwithstanding the enormous effort that has been focused on these noble metal catalysed oxidative dehydrogenations (doping with Bi, Pb, etc.) in water, very few, if any, of these reactions have been used industrially. This is still primarily due to the low selectivity, poor catalytic rate and the extent of metal leaching. A stepwise oxidative dehydrogenation mechanism as shown in scheme 2 has been generally accepted for the oxidation of alcohols by noble metal catalysts [2].



Scheme 2.

Since water is present in a bulk quantity, the aldehyde intermediate is favourably hydrated to a geminal diol and further dehydrogenated to form an acid group. As a result, a low selectivity to aldehyde is therefore obtained at the expense of acid production in the aqueous medium (associated with acid problems).

We now demonstrate that selective oxidation of both water-soluble and insoluble alcohols to carbonyl compounds with high selectivity at high yields by molecular oxygen using simple non-promoted carbon-supported noble metal catalysts can be achieved in $scCO_2$. A water-free non-combustible solvent medium is thus established for the catalysed reactions. No over-oxidation of the alcohols to acids and no apparent metal leaching from the catalysts are now observed. We found no loss of noble metal by post-reaction analysis of the catalytic material (proved by atomic absorption), unlike the aqueous system where the acids produced from the over-oxidation assist in leaching the metal ingredients. The oxidation reaction is less sensitive to gaseous oxygen with respect to deactivation provided that the oxygen level is below the stoichiometric ratio. It therefore seems that $scCO_2$ is a good solvent medium for carrying out aerial alcohol oxidations over noble metal catalysts. However, this work also reveals that it is vitally important to avoid even small quantities of water produced from the oxidation being condensed onto the catalyst pores. In particular, at temperatures below its boiling point water could be strongly adsorbed on the hydrophilic support, filling pores and reducing the effective metal surface for oxidation. Thus, for the catalytic $scCO_2$ oxidation reactions, a hydrophobic surface is necessary to avoid the accumulation of water in the catalysts porous structure and hence the beneficial effects in $scCO_2$ fluid can be fully demonstrated. In addition, aerial oxidation reaction in water is well known to be a slow reaction requiring high catalyst to substrate ratios [2]. Our preliminary results also suggest that the rate of oxidation in $scCO_2$ is considerably higher than the reaction taking place in the aqueous medium. Detailed kinetic analysis of the catalysed reaction is now in progress in our laboratory. We attribute the high catalytic activity and high carbonyl selectivity of the alcohol oxidation reaction to the favourable by-product desorption (e.g., water molecules) from the hydrophobic carbon, and to a better solubility of the less polar carbonyl products and by-products (less polar compared to the alcohol) into the $scCO_2$ fluid. It is also possible that some water entering the $scCO_2$ phase may further modify the hydrophilicity properties of the resulting solvent, hence facilitating some fundamental adsorption or desorption processes on the catalyst surface to/from the $scCO_2$ phase. As a result, it is shown that $scCO_2$ is like organic solvents but is chemically inert to further oxidation (non-combustible) and can exhibit real advantages for the selective oxidation of alcohols. Moreover, $scCO_2$ offers a potential green alternative to the traditional stoichiometric oxidants. It may also provide new opportunities and a stimulus to perform complex chemical (thermal or peroxide labile compounds) oxidation reactions using molecular oxygen at mild temperatures in a safe and controlled manner where no current catalytic method is applicable.

5. Conclusions

This work has elucidated some fundamental aspects of heterogeneous oxidation in supercritical CO_2. The supercritical CO_2 exhibited real advantages for the selective oxidation of alcohols, e.g., 9-anthracene methanol. Unlike the poor catalytic performances of alcohol oxidation in aqueous systems that have been intensively studied, oxidation in $scCO_2$ apparently gave much higher aldehyde selectivity, with no acid formation. The catalyst did not suffer from metal leaching and could be easily recovered. The oxidation process was temperature and pressure dependent due to the "tunability" of the solvent. Being a clean technology, the reaction offers a potential green alternative to traditional stoichiometric oxidants.

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