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Partial aerial oxidation of nonpolar alcohols over Teflon-modified noble metal catalysts in supercritical carbon dioxide

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Abstract

We have reported earlier that modification of commercial graphite Pt-supported catalysts with Teflon fluorinated polymeric coating of a very strong hydrophobic nature can significantly improve catalytic activity for aerial oxidation of water-insoluble alcohols such as *anthracene methanol* in supercritical carbon dioxide ($scCO_2$). Thus, this paper presents some further characterization of these new catalyst materials and the working fluid phase during the catalysis. Using the same Teflon-modified metal catalysts, this paper addresses the oxidation of another water-insoluble alcohol molecule, *m-hydrobenzoin* in $scCO_2$. It is found that conversion and product distribution of this diol oxidation critically depend on the temperature and pressure of the $scCO_2$ used, which suggest the remarkable solvent properties of the $scCO_2$ under these unconventional oxidation conditions.

Keywords: Catalysis; Supercritical carbon dioxide; Noble metal; Partial oxidation; Teflon

1. Introduction

Oxidation reactions are the most important and widely used type of reactions in bulk chemical manufacturing [1,2]. However, as a result of increasingly stringent environmental constraints, industrial-scale oxidation with traditional stoichiometric oxidants such as dichromate or permanganate is no longer acceptable. Consequently, there has been a general trend toward the development of catalytic processes [3–5] that do not generate much effluent/waste. Oxidation of organic molecules using O_2 from air in supercritical carbon dioxide ($scCO_2$) has emerged as one of the most attractive "greener" approaches since air (as the oxidant) and $scCO_2$ (solvent) are both environmentally benign, nontoxic, and inexpensive reagents [6–11]. There has been some attention focused on a number of catalytic aerial oxidations in $scCO_2$ using both homogeneous and heterogeneous catalyst systems. Examples of using heterogeneous catalyst systems in $scCO_2$ include the oxidation of methanol over iron-oxide-based aerogels in $scCO_2$ [7] and the oxidation of octyl alcohols and benzyl alcohol over supported Pd catalysts [8,9]. In particular, an extensive research on catalytic oxidation in $scCO_2$ fluid was carried out by Baiker and co-workers [8,9] who found that their 0.5% Pd solid catalyst was stable without any sign of metal leaching or deactivation within 75 h time-on-stream at the temperature range from 80 to 140 °C in a continuous-flow reactor system. Our preliminary accounting for the oxidation of solid alcohols [10] as well as the work from Gläser and colleagues on the 1- and 2-propanol oxidations [11] using a batch reactor system were also amongst the publications previously reported in this area.

In our previous communication [10], we reported a preliminary account on the selective oxidation of a bulky alcohol, 9-anthracene methanol, by O_2, using a carbon-supported noble metal catalyst (Pt) in $scCO_2$. This substrate, with an extremely low vapor pressure, was deliberately chosen to reveal the major contribution from catalysis in the supercritical phase when it was dissolved therein without

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much influence from the gas or liquid phase under our reaction conditions. We also reported synthesis, testing, and characterization of commercial noble metal catalysts modified with Teflon, which was found to be essential to avoid noticeable catalyst deactivation [10]. In this article, we report an extensive characterization of the Teflon-modified catalytic materials compared with the unmodified commercial catalyst. Also, a direct visualization experiment on the working phase of the fluid is carried out. A brief study on the turnover frequency (TOF) of this reaction under supercritical conditions is also included to shed some light on the role(s) of Teflon coating. Finally, oxidation of a more complex water-insoluble diol compound, *m*-hydrobenzoin, is studied in order to demonstrate that reaction conversion and product distribution could be manipulated by controlling the pressure and temperature of the supercritical fluid over this new type of catalyst, which reveals the validity of this method in application to the area of fine chemical catalysis under mild conditions.

2. Experimental

2.1. Catalyst preparation: noble metal catalyst modification with Teflon

The catalyst used was supplied by Johnson Matthey and consisted of 5% loading of Pt on graphite support. Thus commercial catalysts in new sealed bottles were used without modifications as received. Samples in opened bottles were then stored in a vacuum dessicator prior to use in order to avoid the possibility of water adsorption from moisturized air. Teflon modification on the Pt catalysts was carried out based upon the published method of Hands et al. [12].

2.2. Catalyst characterization

2.2.1. Nitrogen physisorption

The specific surface area (S_{BET}), mean cylindrical pore diameter ($\{d_p\}$), and specific desorption pore volume ($V_p(N_2)$), assessed by the BJH method, were determined by nitrogen physisorption at 77 K, using a Sorptomatic 1990 instrument. Prior to the measurement, samples were degassed at 120 °C for 2 h using a turbomolecular pump. A good dynamic vacuum of $< 1 \times 10^{-8}$ Torr was established over the sample. This drying treatment was found sufficient to remove most preadsorbed water even for highly porous materials (very similar results were achieved over MCM-type materials with more severe drying treatments).

2.2.2. Transmission electron microscopy (TEM)

TEM experiments were carried out using a Phillips CM 20 at 200 kV (0.30-nm point resolution) under bright-field conditions. Samples were prepared by grinding the catalyst with an agate pestle and mortar in isopropyl alcohol. This suspension was then dropped from a Pasteur pipette onto a holey carbon grid and allowed to dry.

2.2.3. X-ray photoelectron spectroscopy (XPS)

XP spectra were recorded on a SCIENTA ESCA 300 system Esca/Auger spetrometer equipped with a hemispherical electron analyzer and an Al-K_α X-ray radiation source ($h\nu = 1486.6$ eV), powered at 12 kV and 10 mA.

2.2.4. CO chemisorption

CO chemisorption was carried out using a commercial Zeton Altamira AMI-200 characterization rig. The sample was prereduced in a flowing stream of dilute hydrogen gas at an elevated temperature. Measurement of the CO chemisorption value was taken at room temperature with pulses of pure CO (100-µl loop size) assuming 1:1 CO to metal sites (valid for Pt nanoparticles from 2 to 1000 nm). It is noted that this measured value represents a modest estimate of the number of metal sites involved in catalysis, which has been based on the assumption that all the surface metal atoms are active.

2.2.5. Visualization of phase behavior through sapphire windows reactor

Experiments were carried out in a ca. 30-ml stainless steel Parr reactor equipped with two high-pressure transparent sapphire windows with a window separation of ca. 4.5 cm. The catalyst and solid substrate were placed in the reactor in order to create the same conditions (65 °C and 150 bar overall pressure) as the 100 ml reactor, where catalysis was performed. The only other difference between the two reactors was the stirring means where the small reactor was stirred by using a magnetic stirrer at the bottom of the reactor. Direct visualization through the sapphire window was carried out to confirm the supercritical state (as a single phase) under the reaction conditions. It is noted that this visualization experiment only reflected the phase properties of the starting mixture. As the reaction proceeded the composition changes might lead to a further change in the phase behaviour that was not addressed by this study.

2.3. Catalytic tests

2.3.1. Oxidation of alcohols in $scCO_2$

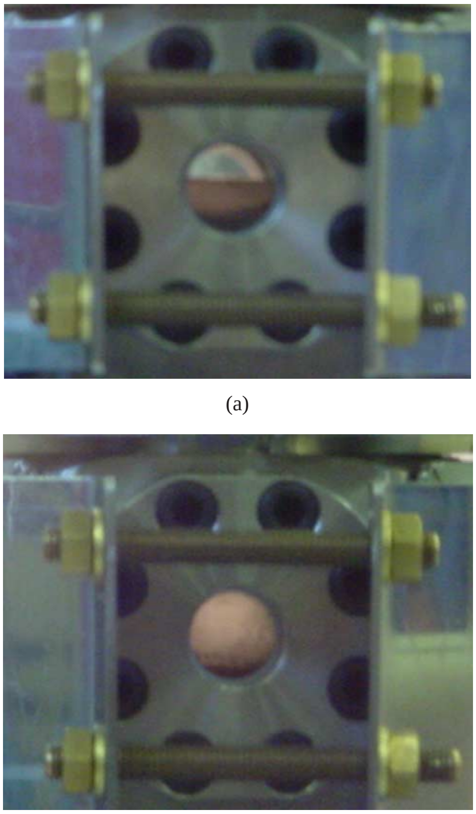
Known quantities of O_2 and CO_2 were delivered to an autoclave system through calibrated digital pressure gauges (Druck plc) in a ca. 100-ml stainless steel autoclave (Parr Instrument, Series 4560 reactor) equipped with a heating jacket and an overhead magnetic stirrer. Typically, initial experiments were carried out by placing catalyst (100 mg dry mass) and solid alcohol substrate (60 mg) in the reactor, which was then closed. O_2 was charged into the reactor directly from the O_2 cylinder (without the O_2 in a direct contact with the booster pump), followed by pumping CO_2 into autoclave using a booster to reach the desired pressure. Stirring was achieved by means of the overhead magnetic stirrer, the motor of which was set at one-half max speed (approx. 360 rpm). It is noted that the temperature of the reactor was raised to 65 °C (∼ 20 min ramping period) before the pressurized CO_2 was actually pumped into the vessel. Such delivery would ensure the CO_2 added as a supercritical fluid rather than as a liquid (condensing liquid CO_2 in a batch reactor could later overpressurize the reactor). There were concerns that the O_2 could overoxidize metal surface prior catalysis. Later experiments showed that the order of adding O_2 was not critically important. As a result, the subsequent experiments were carried out by first adding substrate/catalyst in the reactor (stirred for at least 3 h in preheated $scCO_2$ in order to ensure a complete solubility of the substrate in the mixture) prior to the addition of pure pressurised O_2 directly from the cylinder. At the end of the reaction, the autoclave was allowed to cool down, and the fluid was vented into 50 ml acetonitrile kept at ice temperature. Thereafter, the reactor was opened and the residue was extracted with another portion of the solvent (50 ml). The resulting solutions were combined and centrifuged. Products in solution were analyzed quantitatively by GC (HP5890 system) and HPLC (A Perkin–Elmer HPLC system). The typical mass balance was found to be at about 85–90% using the calibrated HPLC with an internal standard (benzene). A similar trapping efficiency for pure anthracene aldehyde under identical conditions by the cold acetonitrile but without using a catalyst was found. Thus, the selectivity and conversion values were determined taking into account all the recovered products.

3. Results

3.1. Catalytic oxidation of 9-anthracene methanol

3.1.1. Visualization experiments

Due to the limited predictability of theoretical calculations of phase behavior initial experiments were first carried out to ensure that the substrate (9-anthracene methanol), O_2 and CO_2 can be in a single phase under “supercritical state” for chosen reaction conditions. Fig. 1 presents a direct visualization of the fluid through the sapphire windows under different conditions. As can be seen from these pictures, separate phases of liquid CO_2, gaseous O_2, and a solid mixture of Pd catalyst and substrate were clearly visible below the supercritical temperature (room temperature, Fig. 1a). When the temperature is raised to 65 °C at 150 bar, a single-phase transparent fluid was then observed over the solid catalyst with no observed meniscus (Fig. 1b). The observation of a transparent single phase is consistent with the supercritical state already reported in the literature. This clearly demonstrates the complete miscibility of O_2 with $scCO_2$ in a single phase.


(a)

(b)

Fig. 1. Visual inspection through reactor equipped with sapphire windows. (a) A solid mixture of Pt catalyst and anthracene methanol at 25 °C, ∼ 67 bar (with liquid CO_2) where the meniscus is clearly visible; (b) the fluid reaches a transparent supercritical state (windows slightly contaminated with fine catalyst powder) with the disappearance of meniscus at 65 °C, ∼ 150 bar CO_2, 5 bar O_2.

Table 1
Conversion of 9-anthracene methanol and selectivity to 9-anthracene methanal over commercial graphite-supported Pt catalyst with and without Teflon modification

Catalyst	Repeated testing	Conversion (%)	9-anthracene methanal selectivity (%)
5% Pt/G	1	45	> 99
	2	40	> 99
	3	33	> 99
01T5Pt/G (1% Teflon)	1	95	> 99
	2	96	> 99

Conditions: 2.88×10^{-4} mol 9-anthracene methanol, 100 mg 5% Pt/graphite, 5 bar O_2, 65 °C, 150 bar $scCO_2$, 24 h. For the reaction performed in aqueous phase, see Ref. [50].

3.1.2. Catalytic results

Table 1 summarizes the three repeated tests of a commercial 5% Pt/graphite (5% Pt/G) catalyst for oxidation of 9-anthracene methanol in $scCO_2$. Rapidly decreasing conversion for the subsequent testing of the same catalyst, while maintaining > 99% selectivity to aldehyde for all the experiments, was particularly noted. Thus, catalyst deactivation at such a mild temperature is clearly apparent. Notice from the same table that the modification of the commercial catalyst with 1% Teflon can indeed dramatically enhance the reaction conversions while maintaining the $> 99\%$ selectivity to aldehyde. A repeated testing of this modified catalyst does not seem to show any sign of catalyst deactivation. As a result, the hydrophobic Teflon film plays a very interesting role(s) in this catalysis.

3.1.2.1. Influence of Teflon loading Oxidation of 9-anthracene methanol has therefore been carried out using 5% Pt/graphite modified with various Teflon contents (only a brief study without optimising the Teflon content). Results are presented in Fig. 2. As seen, a volcano plot is observed with the increase of the Teflon content on the catalyst. The highest activity (90% conversion) is achieved for 1 wt% Teflon loading. Then, the conversion sharply decreases when the Teflon loading is increased or decreased from 1 wt%. The cause for this interesting volcano activity curve can be elucidated from our catalyst characterizations including XPS, metal surface (CO chemisorption), BET, and pore analyses (Table 2). First, CO chemisorption of the fresh and used samples (Table 2) gave similar metal surface areas. This clearly suggests that no permanent structural modifications occurred on the catalyst. At least, the previously observed deactivation after test for the unmodified catalyst can be reversible in the CO chemisorption measurements (the hydrogen prereduction treatment could reactivate the catalysts). This fact supports adsorption of a kind of polar intermediates and/or by-product(s) that could be the potential reason for the deactivation under mild conditions. Also, the substantially higher activity over the 1% Teflon-coated catalyst than the unmodified catalyst cannot be explained by the increase in number of active sites since 50% of the metal sites are actually lost after the modification (Table 2). It is believed that the dramatic enhancement in activity over the same catalyst is due to the 1 wt% Teflon modification, leading to a significant improvement of the hydrophobic nature of the latter. Consequently, hydrophilic species, such as water molecules produced during the oxidation of 9-anthracene methanol as the co-product could hardly be adsorbed onto the catalyst surface due to the repelling effect of the hydrophobic modified catalyst.

However, it is apparent from the Fig. 1 that Teflon coating also plays a negative role when further increasing in its content onto the catalyst (the conversion dropped abruptly). Our XPS data (Table 2) indicate that the Pt/C ratio decreases dramatically from 0.018 to 0.008 with increasing Teflon loading from 1.0 to 7.0 wt%. Adding only 1% Teflon onto the catalyst led to more than 50% reduction in the metal surface area (3.1 to 1.4 $m^2\ g^{-1}$) with the dispersion decreased from 25.1% to 11.5%. On the other hand, there was only a 23% reduction in the total surface area (contributed mainly from the graphite support) as compared with the raw catalyst. Further addition of 7% Teflon to the catalyst rendered the total loss in the metal surface area. All these observations suggest that the Teflon might not be uniformly covering the catalyst surface but preferably depositing onto the platinum metal over the graphite support. It is difficult to imagine that a specific chemical interaction(s) was created between the inert Teflon polymer fragments and the metal sites. On the other hand, two possibilities may be envisaged: first, selective blockage of the support pores which host small metal particles; second, a kind of induced metal agglomeration leading to a loss in metal surface during the Teflon deposition.

From the N_2 adsorption/desorption measurements, a noticeable decrease in surface areas of the catalysts is observed when the amount of Teflon loading is increased up to 7.0 wt%. Furthermore, careful analysis of the pore distribution of the 1.0 wt% Teflon modified 5% Pt/graphite (designated as 01T05Pt/graphite) compared with the unmodified 5% Pt/graphite indicate a shift of the most frequent pore size from 12 to 10 Å with the decrease in the cumulative volume from 0.224 to 0.200 cm^3/g after the modification. Although the modification effects on pore size and pore volume appear to be rather small, these facts are consistent with the hypothesis that metal sites are predominantly located in the internal

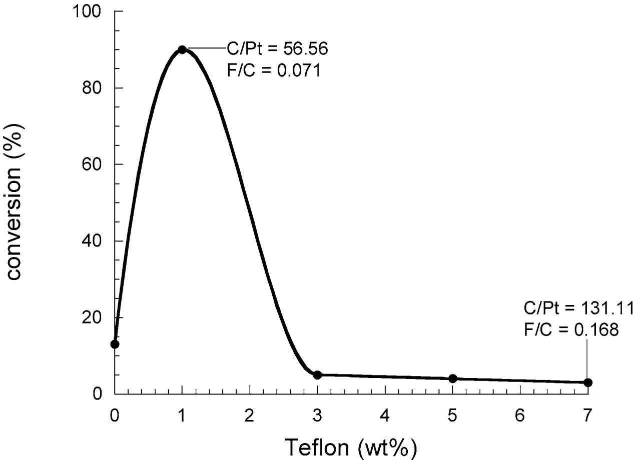


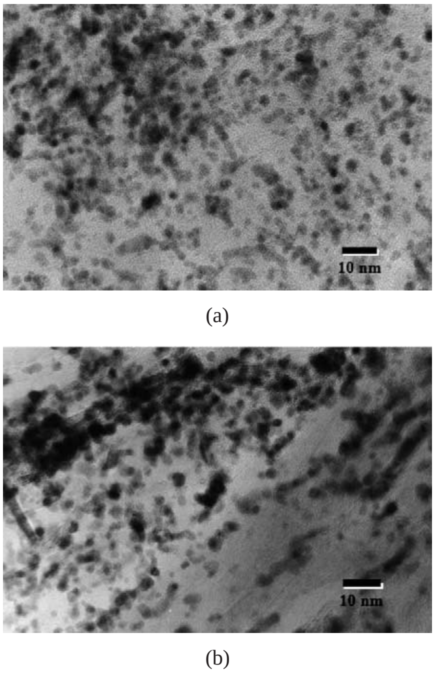
Fig. 2. Plot of the conversion vs Teflon loading for the 9-anthracene methanol oxidation reaction (2.88×10^{-4} mol 9-anthracene methanol, 100 mg modified 5% Pt/G, 5 bar O_2, 65 °C, 24 h, 100% selectivity towards corresponding aldehyde was noted at all Teflon contents).

Table 2
Physicochemical properties of modified 5% Pt/graphite catalysts with different % of Teflon added

Used catalyst	Teflon (wt%)	Pt metal surface area ($m^2\ g^{-1}$)	Pt dispersion (%)	BET surface area ($m^2\ g^{-1}$)	XPS	
					Pt/C	F/Pt
5% Pt/G[a]	0	3.1	25.1	124		
5% Pt/G	0	3.2	25.8			
01T5Pt/G[b]	1	1.4	11.5	95	0.018	4.0
01T5Pt/G	1	1.3	11.0			
03T5Pt/G	3	–	–	68		
05T5Pt/G	5	–	–	52		
07T5Pt/G	7	Nil	Nil	40	0.008	22.1

[a] 5% Pt/G stands for fresh 5 wt% Pt on graphite before test.

[b] 5% 01T5Pt/G stands for fresh 1 wt% Teflon, 5 wt% Pt on graphite before test.



(a)

(b)

Fig. 3. (a) TEM image of 5 wt% Pt/graphite; (b) TEM image of 5 wt% Pt/graphite modified with 1 wt% Teflon.

pores that could be favorably blocked by the Teflon deposition. TEM images (Figs. 3a and 3b) demonstrate that there was indeed some degree of Pt particle agglomeration after the Telfon modification. Thus, the selective loss of metal sites could be due to the combination of these two possibilities. One important fact derived from this work is that the Teflon modification creates a dual effect. On one hand, the selective coverage of metal sites with a Teflon coating can substantially reduce catalytic activity (covering the metal sites), but the gain in hydrophobicity can compensate for the loss in activity. Thus, careful optimization is required to introduce the hydrophobic character of the resulting catalyst without severely burying the metal sites.

3.1.2.2. A study in reaction rate In order to gain insight into the mechanism of the 9-anthracene methanol oxidation over the 1% Teflon modified 5% Pt/graphite catalyst, the substrate conversion versus time and the corresponding plot in $\ln C_0/C$ vs time were obtained at a large molar excess of O_2 (23 × excess). Each point was collected by quenching the reaction mixture in the batch reactor immediately to room temperature at different reaction times (using a fresh catalyst/substrate at each point). Results are presented in Fig. 4.

As can be seen from the figure, 75% of 9-anthracene methanol is converted within the first 15 h of the reaction, and further time leads to a limited increase of conversion. From this figure, at the initial 9-anthracene methanol conversion, the turnover frequency (TOF) of the reaction can be deduced. Also, based on the conversion-time curve, a derivation of a kinetic equation for a first-order reaction is represented as

$$\ln(C_0/C) = kt, \tag{1}$$

where C_0 and C are the initial concentration and the concentration of the substrate after a reaction time of t hours, respectively, and k is the rate constant.

As can be seen from Fig. 4 (right), a straight line is indeed obtained, which suggests that the reaction is first order with respect to the 9-anthracene methanol within experimental error. The slope of this straight line gives the constant k, which is calculated to be $8.83 \times 10^{-2}\ \mathrm{h}^{-1}$. Taking the substrate ($1.735 \times 10^{20}$ molecules) and available surface metal sites (1.775×10^{18} surface metal sites evaluated from CO chemisorption in the 100 mg catalyst) into account, the TOF is determined to be $8.63\ \mathrm{h}^{-1}$ (based on exposed Pt sites), with no induction period being observed.

3.2. Catalytic oxidation of *m*-hydrobenzoin

A brief study of catalytic aerial oxidation of *m*-hydrobenzoin was carried out over the same 1% Teflon-promoted

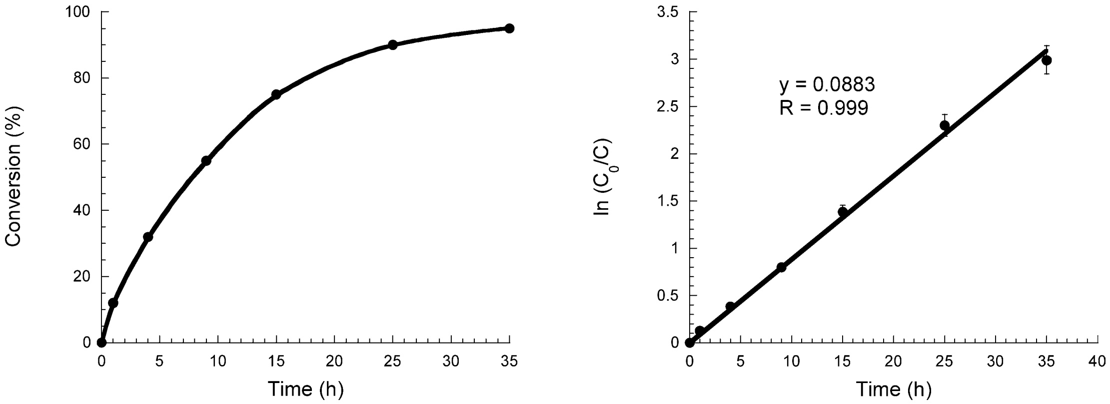
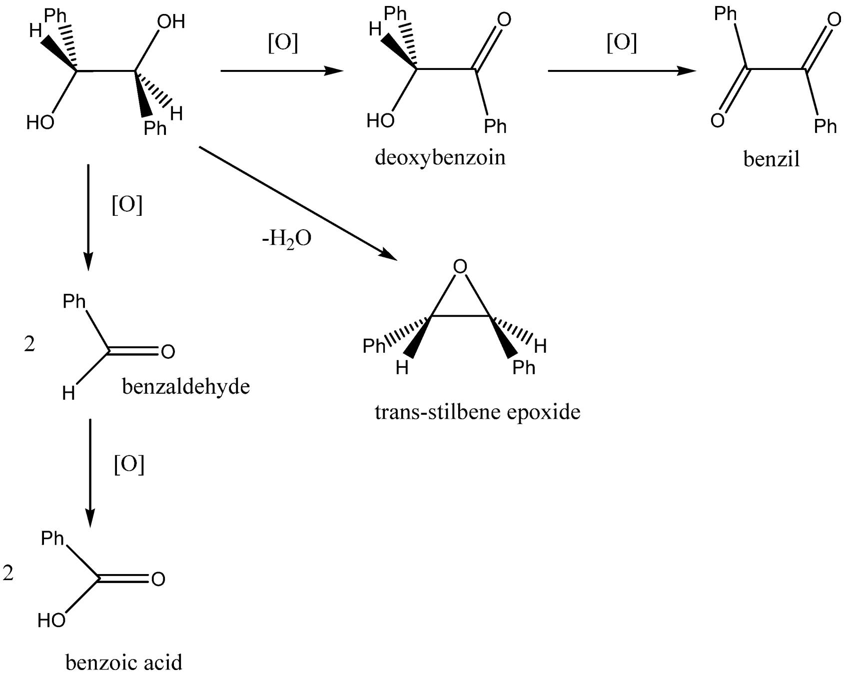


Fig. 4. (left) Conversion vs time for the oxidation of 9-anthracene methanol; the derived plot of the initial conc. to measured conc. ratio, C_0/C, of the substrate vs time (right) (2.88×10^{-4} mole 9-anthracene methanol, 100 mg of 01T5Pt/G, 5 bar O_2, 65 °C, 150 bar $scCO_2$. Under these conditions 100% selectivity toward corresponding aldehyde was noted over all different times; the time zero was defined as the true when O_2 was added into the mixture after a steady state was achieved. Each data point was collected by quickly quenching (in a running water jacket with < 20 min. cooling time) and analyzing the reactor contents to minimize the catalysis contributions from nonsteady periods).



Scheme 1. Reaction pathway for the *m*-hydrobenzoin oxidation.

Table 3
Oxidation of *m*-hydrobenzoin in $scCO_2$: influence of temperature and pressure

Condition	Conversion (%)	Product distribution (%)				
		Epoxide	Deoxybenzoin	Benzil	Benzaldehyde	Benzoic acid
60 °C, 110 bar	17	**56.3**	14.4	19.9	9.1	0.4
80 °C, 100 bar	42	10.2	0.5	**63.3**	25.8	0.2
80 °C, 150 bar	78.8	7.2	21.6	43.9	26.1	1.2
80 °C, 180 bar	99.0	6.8	33.7	33.7	26.4	2.1

2.81×10^{-4} mol *m*-hydroxybenzoin, 100 mg 01T5Pt/G, 5 bar O_2, 65 °C, 24 h.

Pt catalyst in order to investigate the solvent effects of the $scCO_2$. The reaction pathway of *m*-hydrobenzoin oxidation is presented in Scheme 1. As seen, oxidation of *m*-hydrobenzoin can lead to the formation of numerous products, due to its facile and specific structure. Under our conditions, *trans*-stilbene epoxide, deoxybenzoin, benzyl, benzaldehyde, and benzoic acid were detected as the major products. Table 3 presents the *m*-hydrobenzoin conversions and product distributions as a function of both temperature and pressure. One can classify three routes (arbitrarily assigned as parallel routes) to produce these products, namely oxidative dehydrogenation of *m*-hydrobenzoin to form deoxybenzoin and subsequently benzil (these routes are catalyzed by the surface of a noble metal catalyst in air); oxidation cleavage of C–C bonds leading to benzaldehyde and then benzoic acid (facile nature of the C–C bond associated with the two Ph pedant groups); and dehydration of the *m*-hydrobenzoin to *trans*-stilbene epoxide.

Using similar pressure of $scCO_2$, the increase of the reaction temperature leads to an increase of the *m*-hydroxybenzoin conversion, but more interestingly, a complete change of product distribution is noted. (This could be partly due to the inverse relationship between conversion and selectivity.) Indeed, a small amount of *trans*-stilbene epoxide, which is the main dehydration product of *m*-hydroxybenzoin (56.3%), presumably formed from its small vapor pressure at 60 °C (for pure $scCO_2$ the density would be about 0.3 $g\,cm^{-3}$, thus low density of this fluid with a low solvency is expected [13]), decreases to 10.2% selectivity at 80 °C, whereas in the meantime, selectivity to oxidative dehydrogenated products (known to be favorable at elevated temperatures), especially the benzil, increases up to 63.3%. When the reactions were carried out at 180 bar $scCO_2$ at the same temperature (for pure $scCO_2$ the density would be about 0.55 $g\,cm^{-3}$, thus higher density with better solvency of the fluid is expected [13]), a dramatic increase in the conversions with an almost completion in conversion was observed. This observation agrees well with our previous results in the oxidation of 9-anthracene methanol [10] as well as those shown in the literature suggesting an increase in pressure will result to an increase in solvent properties [8,9,14]. It is interesting to notice that a rough plot of the conversion vs pressure gives a straight line. By enhancing the solvency of the fluid, more solid substrate would be able to enter into the fluid phase; hence a higher substrate to O_2 ratio will be in contact to the catalyst surface. For noble-metal-catalyzed oxidation, availability of O_2 and organic sources to metal surface is well known to affect reaction activity and selectivity. There seemed to be no major change in the selectivities of the oxidatively cleaved products (benzaldehyde and benzoic acid) once the temperature reached 80 °C at different pressures (different substrate-to-O_2 ratios in the fluid phase). However, higher selectivities were found toward the partially oxidized product deoxybenzoin at the expense of the fully oxidized product benzil at higher substrate-to-O_2 ratios (at higher pressures). Thus, for the chosen alcohol oxidation, it is very interesting to observe the dramatic change in both activity and selectivity of the reaction by modifying the solvency of the supercritical phase via pressure and temperature alternations.

4. Discussion

As already stated, there is an increasing demand to use O_2 from air as an oxidant for industrial oxidation processes with regards to process economy and reduced environmental impacts. However, air oxidation of fine organic molecules in organic solvents is industrially not preferred, since vigorous oxidation could cause overoxidation of the bulk organic solvent, leading to explosions [6]. Thus, water has always been the favored option for the oxidation of water-soluble alcohols, but water-insoluble compounds remain the main problem. Even so, it is well known that the presence of bulk water unfortunately leads to rapid formation of geminal diols on metal surface from water-soluble alcohols, which will further undergo dehydrogenation to form an undesirable acid product [6]. With the $scCO_2$ as the solvent medium, this problem is apparently overcome; in particular, no bulk water phase will be in contact with the metal surface. Thus, in the oxidation reaction of 9-anthracene methanol, higher selectivity to corresponding aldehyde was indeed found when $scCO_2$ was used as the solvent. This result clearly demonstrates the beneficial effect of this new environmentally friendly “solvent” both in term of product distribution and in term of enhanced conversion.

However, from this work we also note a new scenario in the alcohol oxidation in the $scCO_2$. The $scCO_2$, being a very nonpolar solvent with a poor ability to dissolve polar species, is rather difficult to use to remove polar products or by-products formed from the catalyst surface due to incompatibility in hydrophilicity/hydrophobicity. This is a very important point since the oxidation reaction will alter the polarity of organic compounds drastically, especially when O_2 is inserted into the molecules. Polar intermediates or by-products, such as water molecules as a co-product, are commonly produced from oxidation reactions. Their formation over a catalytic surface relatively hydrophilic compared to the nonpolar $scCO_2$ prevents their desorption to the nonpolar fluid phase, leading to potential catalyst deactivation, as readily observed in our case. It is noted that there are very limited options for altering the relative hydrophilicity of $scCO_2$, since the uses of organic co-solvent(s) and elevated temperatures reduce the attraction of this new solvent with regard to environmental impacts and safe operation for metal-catalyzed oxidation reactions. In contrast, reported work on using unmodified Pt/alumina catalysts (presumably the catalyst is more hydrophilic than our carbon-supported catalysts) for the air oxidation of octyl alcohol in $scCO_2$ [8,9] does not seem to suffer from rapid catalyst deactivation under their continuously flowing reactor system. We therefore believe that this catalyst deactivation could perhaps be more pronouncedly noticeable at low operating temperatures in a batch reactor system similar to our system, where there is no escape in the build up of the polar species during the oxidation. It is noted that water molecules are attributed as the cause for the deactivation; however, other polar species/intermediates cannot be discounted. In the absence of identification of other hydrophilic species, the water molecule is the prime suspect. It is noted that a small quantity of water is required to block the small pores. Accurate analysis of water from the catalysts with and without the Teflon modification cannot easily be carried out. Nevertheless, the important point is that one should be cautious on the compatibility of solvency and polarity of species involved when mild temperatures, suitable for oxidation of thermally labile multifunctional complexes of fine/pharmaceutical chemicals, are adopted. Thus, $scCO_2$ as a solvent offers new opportunities as well as new limitations. To overcome this limitation the noble metal catalyst was modified with a Teflon coating. The results showed a significant improvement for 9-anthracene methanol oxidation. This improvement can be accounted for by improvement in the hydrophobic character of the Teflon-modified catalyst, which prevents the absorption of polar species, i.e., prevents water formed during the oxidation process from being retained on the catalyst surface. However, it is also clear from our catalyst characterizations that the amount of Teflon loaded must be carefully controlled, as our results indicate that overloading of the Teflon coating can lead to a dramatic decrease of catalytic activity due to selective covering of the active metal sites (blocking pores where metal is located) by the Teflon. From the study of reaction rate, we have also demonstrated that the reaction is first-order with respect to 9-anthracene methanol. This observation is consistent with similar observations made in detailed kinetic analyses of metal-assisted oxidation reactions, which suggested that initial dehydrogenation of alcohol onto metal surface is likely to be the rate-limiting step in the alcohol oxidation [6]. Surprisingly, a rather low turnover frequency of 8.63 h^{-1}, based on Pt, over our 1 wt% Teflon-promoted 5% Pt/graphite catalyst was obtained at 65 °C, 150 bar $scCO_2$, as compared to the recent reported TOF of 1.585 h^{-1} for the oxidation of benzyl alcohol over 0.5% Pd/alumina catalyst at 80 °C and 150 bar $scCO_2$ in a continuous flow system [15]. Despite taking this value too literally, there is a significant difference (more than two orders of magnitude) in the TOF value we measured compared with the literature value (different alcohol). We believe that the discrepancy could be due to a combination of possible reasons. First, our substrate molecule is different from the reported benzyl alcohol, which is a volatile liquid, whereas our 9-anthracene methanol is a solid under reaction conditions. Thus, one could argue that there could be contributions from direct vapor-phase as well as liquid-phase catalysis when the substrate was dosed into the flowing stream of $scCO_2$ in the case of the benzyl alcohol oxidation. For solid 9-anthracene methanol, this substrate could only be available to the catalyst when dissolved in $scCO_2$. On the other hand, there is no published data on the solubility of 9-anthracene methanol nor is there any reliable theoretical prediction of this value. Thus, we cannot discount the possibility that a slow rate is encountered due to a slow equilibrium to solution at the excess solid 9-anthracene methanol to bring it into contact with the catalyst despite the fact that a small quantity is deliberately placed. Work is in progress to compare catalytic oxidative activity in $scCO_2$ using both batch and continuous reactors under comparable conditions.

Concerning the m-hydrobenzoin oxidation reaction over the Teflon-modified Pt/graphite, our preliminary results are both encouraging and stimulating. However, it should be noted that there is no intention to suggest this reaction in supercritical fluid can deliver the best activity or selectivity. Notice that glycol oxidation using a Au/C catalyst in a vapor phase has been cited as achieving a nearly 100% selectivity toward aldehyde [16]. The main point derived from this work is that the activity and selectivity could be manipulated by adjusting the pressure and temperature of this new fluid. For a network of parallel or competing surface reactions, it is known that the different availability of chemical species transported from the fluid phase to the metal surface, as well as the different activation volume ΔV associated with each activated complex, constitute the overall pressure/temperature effects on each of the elementary rate constants, giving different overall selectivity [17]. Under subcritical multiphase conditions manipulation of these reaction extents is impaired by the different behaviors exhibited by the phases. However, we show clearly that manipulation of reaction activity and selectivity of the m-hydrobenzoin oxidation can be made possible under our supercritical conditions where the reaction mixtures are in a single phase. Using a solid substrate it is also shown that its concentration, in turn affecting the substrate/ O_2 ratio, can be controlled by changing the solvency of the fluid (temperature and pressure). It is worth pointing out that Arai and co-workers [18] have also recently reported an interesting CO_2 pressure effect on the selectivity of unsaturated alcohol in the hydrogenation of cinnamaldehyde over Pt/Al_2O_3.

5. Conclusion

It is revealed that polar/hydrophilic incompatibility of the supercritical fluid with the polar product(s) such as water produced from oxidation with respect to the catalyst surface could lead to a rapid catalyst deactivation. To overcome this problem, we report synthesis, testing, and characterization of new Teflon-coated noble metal catalysts, which can be optimized to be active for catalyzing aerobic oxidation of alcohols in $scCO_2$ without noticeable deactivation. We also demonstrate that temperature and pressure are important experimental parameters to influence activity and selectivity in the m-hydrobenzoin oxidation in $scCO_2$ fluid over this type of Teflon-modified Pt catalyst. The pressure and temperature are expected to affect elementary surface reactions during m-hydrobenzoin oxidation over Pt catalyst, giving rise to different products.

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