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Effect of Temperature and Pressure in the Photocatalytic Oxidation of *n*-Octanol on Partially Desilanized Hydrophobic TiO$_2$ Suspended in Aerated Supercritical CO$_2$[†]

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Reaction temperature and CO$_2$ pressure affect the rate of reaction in photocatalytic oxidations in supercritical (sc) CO$_2$ on partially silanized TiO$_2$. In supercritical CO$_2$, the photocatalytic oxidation of octanol appeared to follow pseudo-first-order kinetics, with octanal being produced as the initial product. At 309 K, the pseudo-first-order rate constant k_{dis} decreased upon increasing CO$_2$ pressure from 8 to 20 MPa, giving rise to an increased yield of octanal. When the temperature was raised within the range from 299 to 319 K at constant CO$_2$ pressure (10 MPa), k_{dis} increased while the net yield of octanal decreased. These changes are rationalized as being caused by changes in near-surface CO$_2$ density and, hence, in efficiency of mass transport of octanal to and from the catalytically active site. The observed dependence of the photoactivity of hydrophobic T805 TiO$_2$ in scCO$_2$ on temperature and pressure likely varies with surface conditions promoted by irradiation, which effects partial desilanization photocatalytically active sites. When scCO$_2$ density was very low, T805 TiO$_2$ did not suspend well into the scCO$_2$ fluid; that is, almost all of the T805 TiO$_2$ precipitated on a window or inner wall of the cell. At scCO$_2$ densities between 8 and 20 MPa, T805 TiO$_2$ was efficiently dispersed under stirring. At very low pressures near the critical point, the kinetic analysis was complicated by incident light scattering caused by suspended particles which act as inhibitory inner filters.

Introduction

Metal oxide semiconductor photocatalysis is useful as an advanced oxidation technique because of its utility in the oxidative degradation of pollutants present in air or wastewater.[1,2] Photocatalysis has also proved to be a useful technique for selective oxidation reactions, although achieving a synthetically useful yield requires some means to remove the initial oxidized product from the active surface.[2–4] In TiO$_2$ photocatalysis, an electron (e$^-$)/hole (h$^+$) pair is produced upon irradiation with incident light of energy greater than the band gap.[1–7] The valence band h$^+$ is trapped by an electron donor, often adsorbed H$_2$O or OH groups on the surface of TiO$_2$ in aqueous media or by an adsorbed oxidizable substrate in nonaqueous solvents. Hole trapping thus produces a hydroxyl radical (OH•) or a singly oxidized species, respectively. A surface-bound OH• can attack pollutants rapidly when they are at or near the surface,[1–7] producing either a OH adduct, a radical, or the same single electron oxidized species formed by direct interfacial electron transfer from the adsorbate. Because these two routes feature different roles for OH•, the course of photocatalytic degradation can follow a quite different mechanistic course in aqueous and nonaqueous solutions. It is interesting therefore to characterize mechanistic differences characteristic of photocatalysis conducted in other nonaqueous media.

Supercritical fluids (SCF) have also been examined as alternative solvents for reactions seeking environmental reme-

diation of organic pollutants. SCFs can achieve selective extraction of a desired material from a mixture of compounds, and their physical properties can be easily controlled by adjusting temperature and pressure. Because supercritical CO$_2$ (scCO$_2$) is nontoxic and nonflammable and because supercritical fluid conditions are easily reached in normal laboratories (critical pressure and temperature are 7.38 M Pa and 304 K, respectively),[8,9] scCO$_2$ might logically be viewed as a particularly attractive fluid for heterogeneous photocatalysis.

Thus, we have studied the photocatalyzed decomposition of *n*-octanol as a model organic compound by TiO$_2$ oxidative photocatalysis in aerated scCO2.[10] We have found that hydrophobic TiO$_2$, Degussa T805, is suitable as a photocatalyst in scCO$_2$,[10] and the observed induction period associated with controlled oxidative reactivity likely results from partial desilanization, as has been described previously by our group.[3,10] Thus, with T805, an active site is itself hydroxylated, but also surrounded by a highly nonpolar local environment from neighboring silanized sites. We report here our description of the effect of pressure and temperature on observed photocatalytic activity of this interesting photocatalyst near the critical point of the fluid.

Experimental Section

Materials. T805 TiO$_2$ powder was used as received (Degussa).[11] Because T805 TiO$_2$ is prepared by modifying P25 TiO$_2$ with trimethoxyoctyl silane, the surface of T805 TiO$_2$ is hydrophobic. Like P25, T805 TiO$_2$ has a BET surface area of about 50 m^2 g^{-1} and a morphology of 70% anatase and 30%

rutile crystalline phase.[11] Desilanization by irradiation of T805 in aerated scCo₂ is established by the appearance of −OH stretches in the IR spectrum.[10]

CO_2 (Holox, minimum purity 99.99%) and O_2 gas (Holox, minimum purity 99.5%, H_2O < 5 ppm) were passed through a moisture trap (Agilent Tech., model MT-4-SS) before being transferred to the reaction vessel. Other chemical reagents, including *n*-octanol and *n*-octanal (Aldrich, 99+% ACS grade), were used as received.

High-Pressure Vessel. The photocatalytic oxidation of octanol on T805 suspended in $scCO_2$ was carried out in a high-pressure reaction vessel (inner volume of 15 mL) made from A316 stainless steel. This high-pressure vessel includes an internal flow loop to control the fluid temperature and four sapphire windows with an absorbance cutoff of 200 nm. It is thus suitable for optical observation of changes in the composition of the fluid solution by normal absorption techniques. The details of construction and operation of the high-pressure vessel have been described previously.[12]

Photocatalytic Reaction. T805 TiO_2 powder (50 mg) and 0.08 mmol of octanol were inserted into the high-pressure vessel. The sealed vessel was placed on a magnetic stirrer and was connected to a gas chromatograph (GC) (Hewlett-Packard, 5890) equipped with an HP-5 capillary column (0.25 mm × 25 m) with helium as the carrier gas. This GC was connected to the six-port valve of the autogas injector (Valco Instruments E60). CO_2 gas containing O_2 at 0.2 MPa as a gaseous mixture was pumped into the high-pressure vessel at room temperature with an HIP pump (High-Pressure Equipment Co., 87-6-5, 60 cm³/ stroke). The final total gas pressure was adjusted from 6 to 20 MPa. The reaction temperature was controlled from 289 to 329 K by circulating a preequilibrated ethylene glycol−ethanol mixture. The T805 TiO_2 powder suspended in $scCO_2$ was stirred for about 30−60 min before irradiation.

In the present study, the observed photocatalytic activity was insensitive to initial O_2 pressure when the initial pressure ranged from 0.2 to 1 MPa. To maintain an excess of O_2, a fixed O_2−CO_2 mixture was introduced into the vessel, and the total pressure was adjusted by adding pure CO_2.

The light source was a 100 W Hg−Xe lamp (ORIEL Co., model 7340). Excitation wavelengths below 300 nm were removed by a cutoff filter (Newport Co.) to eliminate direct photolysis of octanol or any reaction intermediate. The excitation light was condensed by a quartz-focusing lens focused to the center of the cell. Further experimental details about such photolyses have been described previously.[10]

Photocatalytic activity was monitored by sampling the reaction mixture composition by opening the valve to the autoinjector at 1-h intervals after starting the irradiation. Because the CO_2 pressure was lowered at each sampling, a defined quantity of CO_2 was added to the reaction vessel to maintain the desired CO_2 pressure after each sampling. The GC line was flushed with compressed air or nitrogen after each sampling to remove octanol and other reactant remaining in the gas line or the six port sampling system.

Physical Properties of CO_2. The supercritical fluid properties of CO_2 are influenced by pressure and temperature, with the density of the sc fluid in appropriate ranges correlating directly with temperature and pressure changes. The sc fluid density was calculated from the Peng−Robinson equation of state which estimates near-surface density and solubility of various reactants into either single-phase or multicomponent mixtures.[12−14] Figure 1 represents the effect induced by a range of temperatures on total fluid CO_2 density as a function of applied pressure.
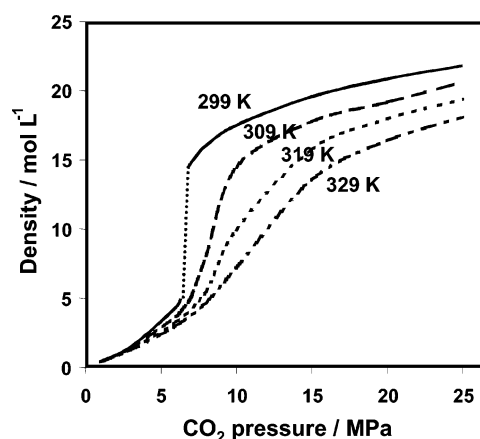

Figure 1. Dependence of near-surface CO_2 density on pressure at 299, 309, 319, and 329 K calculated by the Peng−Robinson equation of state for pure supercritical CO_2.[12−14]
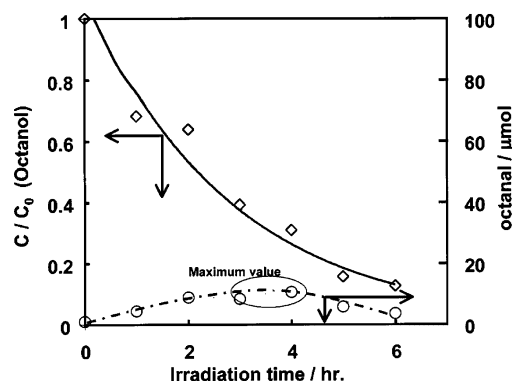

Figure 2. Photocatalyzed disappearance of octanol and the appearance of octanal in aerated $scCO_2$ as a function of irradiation time on T805. CO_2 pressure and cell temperature: 10 MPa and 309 K, respectively.

Results and Discussion

Photocatalytic Oxidation of Octanol in $scCO_2$. In the absence of O_2, octanol is degraded only very inefficiently upon irradiation of T805 suspended in $scCO_2$, with a CO_2 pressure and cell temperature of 10 MPa and 309 K, respectively. Only octanal was detected, with less than 1% disappearance of reactant after 7 h irradiation. In the dark in the presence of O_2, no reactivity was observed on T805. Only upon UV irradiation in the presence of O_2 was efficient photocatalytic oxidative degradation of octanol observed.

Although it has been reported that photocatalytic reduction of CO_2 can be induced upon irradiation of TiO_2 at high CO_2 pressures,[15] no evidence for partial reduction products could be detected over the shorter irradiation periods of our experiment, with or without fluid aeration. Thus, the oxidative photocatalytic degradation of octanol in the presence of O_2 is at least 50 times more efficient than any possible photocatalytic reduction of CO_2 under the same conditions. This difference derives from the ability of oxygen to greatly enhance photocatalytic reactivity by acting as an electron trap. A plot of the disappearance of octanol upon photocatalytic oxidation on T805 in aerated $scCO_2$, together with a plot of the appearance of octanal, both as a function of irradiation time, is shown in Figure 2.

The initial photocatalytic oxidation was observed to follow roughly a first-order rate kinetic profile. That the rate of the photocatalytic oxidation can be so fit indicates that the oxidation of octanol in $scCO_2$ is mass-transfer controlled.[16] This rate, in turn, is significantly influenced by near-surface CO_2 density,

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which is affected by pressure and temperature. The near-surface fluid density is known to affect observed diffusion coefficients and solubilities in scCO$_2$.[8]

Limitations on Photocatalytic Activity in scCO$_2$. When the CO$_2$ pressure was adjusted beyond the maximum temperature and pressure (20 MPa at 319 K), T805 powder precipitated onto the sapphire window, despite constant stirring of the suspension. The T805 powder became fully suspended, however, in scCO$_2$ upon irradiation for about 30−60 min under stirring, likely because of partial desilanation.[10] At even lower CO$_2$ pressure (6 MPa), complete T805 powder dispersion into scCO$_2$ could not be observed even after 9 h irradiation with stirring.

A similar changing of suspension condition was also observed with P25 TiO$_2$ in scCO$_2$, but the ability to obtain a stable suspension was much lower on P25 than on T805 when the CO$_2$ pressure and cell temperature were 10 MPa and 309 K. Therefore, it seems likely that adsorption and accumulation of octanol, octanal, and other intermediates on the surface of TiO$_2$ (both T805 and P25) may affect the stability of the photocatalyst dispersion.

Continual removal of all silanol groups from the oxide surface of T805 by photodesilanization inhibits photocatalyst dispersion but produces an activity profile nearly identical to that seen with P25 TiO$_2$ powder.[19] The desilanized photocatalyst is hydrophilic and nonpolar scCO$_2$ poorly solvates its surface. Therefore, continued photodesilanization induces partial flocculation of the increasingly hydrophobic T805 TiO$_2$ particles suspended in scCO$_2$, mitigating against dispersion of the active photocatalyst. Thus, changes in scCO$_2$ fluid properties and T805 surface conditions are key in producing photocatalytic oxidation products.

We have also observed a change in the color of the suspended T805 in scCO$_2$ upon irradiation, changing from translucent white (turbid) to light yellow during the photolytic desilanization induction period when CO$_2$ pressure and temperature ranged from 10 to 20 MPa and 299 to 309 K, respectively. When the stirring was stopped, the filtered T805 photocatalyst appeared to be white. If conduction band electrons had accumulated in the photocatalyst, a blue color attributed to the formation of Ti^{3+} might have been expected, but no such color change was evident.[20] More likely, the observed changes in color of the T805 suspension in scCO$_2$ might result from light scattering.

We conclude, therefore, that the surface hydrophobicity of T805 suspended in scCO$_2$ directly affects the efficiency of the photocatalytic degradation rate of octanol in aerated scCO$_2$. Although T805 powder can be dispersed by preirradiation under stirring, the suspended particles can still scatter incident light.[21]

Effect of CO$_2$ Pressure. To determine the effect of CO$_2$ pressure on the efficiency of T805 photocatalytic oxidations on scCO$_2$, the cell pressure was adjusted in the range from 6 to 20 MPa at 309 K. The effects of these pressure variations on the observed initial reaction rate showed that the pseudo-first-order rate constant k_{dis} decreased with an increase in CO$_2$ pressure, Figure 3. An increase in CO$_2$ pressure in this region can displace a multicomponent layer adsorbed on or formed at the desilanized hydroxylic active site of the suspended photocatalyst, thus diminishing the possible role of physisorbed H$_2$O, hydrogen-bound octanol, or other oxidizable substrates.[8]

Because the distinction between bulk gas and liquid at or near the surface of the catalyst disappears in scCO$_2$, the rate of mass transfer of a dissolved substrate can be significantly enhanced,[8] along with the solubility of any nonpolar solutes. Consequently, CO$_2$ pressures at or above critical point will initially shift the surface composition toward oxidation product.
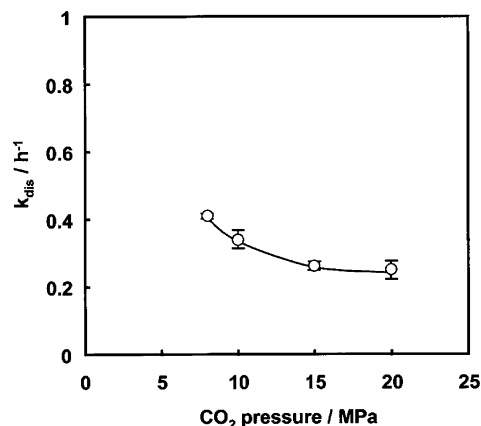

Figure 3. Dependence of k_{dis} on initial CO$_2$ pressure in the photocatalytic degradation of octanol on T805 suspended in aerated scCO$_2$. Temperature: 309 K. Plotted values are averages obtained from three repeated experiments.
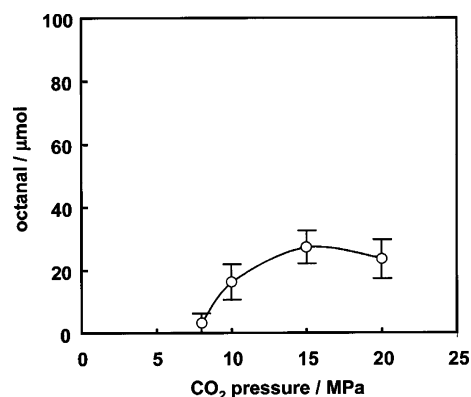

Figure 4. Dependence of maximal photocatalytic oxidation on silanized TiO$_2$ (T805) in aerated scCO$_2$ of octanol to octanal on initial CO$_2$ pressure. Temperature: 309 K. Plotted values are absolute yields produced in a 15-mL cell, reported as averages of three experiments.

Therefore, the observed decrease in k_{dis} can be rationalized as having been derived from the less polar photocatalytic oxidation products accumulating at the fluid surface of the hydrophobic T805 particle. This result reflects changes in the near-surface solvent density and in the adsorption equilibrium constant for octanal. Thus, mass transfer of the reactant and products to and from the surface-activated photocatalytic site likely controls the course and rate of photocatalytic degradation. In previous work in supercritical CO$_2$,[10] weak dependence of k_{dis} on total pressure was also observed.

Absolute confidence in this interpretation would require full independent determination of partition coefficients for the reactant and product as a function of near-surface density. In turn, this would require determination of adsorption isotherms as an evolving function of octanol/octanal mixtures, using binary phase diagrams for each species as a function of fluid composition. Such a determination will be pursued in future work but is beyond the scope of the current study.

The concentration of the primary oxidation product (octanal) reached a maximum at about 3−4 h of irradiation time, Figure 2. In Figure 4, the maximum production of octanal is plotted as a function of fluid CO$_2$ pressure. Thus, the yield of octanal increased with CO$_2$ pressure from 8 to 15 MPa, even as k_{dis} decreased slightly, Figure 3. Because the aldehyde produced is more hydrophobic than its more polar precursor alcohol, a higher CO$_2$ pressure will cause it to desorb more easily from the catalytically active surface site than does the more tightly hydrogen-bound alcohol. Thus, mass transport of octanal from
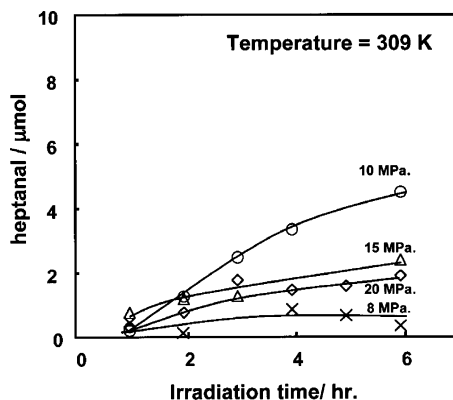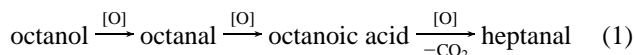
Figure 5. Photocatalyzed production of heptanal from *n*-octanol on irradiated silanized TiO₂ (T805) in aerated scCO₂ as a function of irradiation time. Temperature: 309 K. Plotted values are absolute yields produced in a 15-mL cell, reported as an average of three experiments.

Figure 6. Photocatalyzed production of octanoic acid from *n*-octanol on silanized (T805) TiO₂ in aerated scCO₂ as a function of irradiation time. CO₂ pressure and temperature: 20 MPa and 309 K, respectively. Plotted values are absolute product yields produced in a 15-mL cell, reported as average data from three experiments.

Figure 7. Dependence of k_{dis} on reaction temperature in the photocatalytic degradation of octanol on T805 suspended in aerated scCO₂. CO₂ pressure: 10 MPa. Plotted values are averages obtained from three experiments.

the TiO₂ surface into the bulk supercritical fluid is facilitated at higher CO₂ density.

At 6 MPa of CO₂ pressure, only small quantities octanol and octanal were observed, presumably because the photocatalyst is only poorly suspended in scCO₂ at such a low CO₂ density (Figure 1). Increasing pressure brings enhanced solubility and, hence, better mass transfer of the reactant from the bulk fluid to the photocatalytically active site. At 20 MPa of CO₂ pressure, the yield of octanal was roughly the same as at 15 MPa, likely because of a balance between increased production of initial and secondary oxidation products deriving from rising CO₂ pressure and an enhanced mass transport to and from the catalytically active surface, Figure 3. The net result is that photocatalytic activity then reaches a rough plateau. An apparent plateau would also be expected because larger fluid density changes are observed upon adjusting the supercritical fluid total pressure from 8 to 10 MPa than from 15 to 20 MPa. There is no evidence that the photocatalyst is differentially suspended within this pressure range, that is, there is no evidence of precipitation from direct optical or light scattering measurements between pressure of 8 to 20 MPa.

The production of small amounts of heptanal could also be observed when CO₂ pressure was varied between 10 and 20 MPa at 309 K, Figure 5. When the applied pressure was dropped to 8 MPa, the observed production of heptanal drastically decreased, illustrating that unexpectedly large changes are provoked by local solvent density changes near the critical point.

Heptanal is likely formed by photocatalytic oxidation of octanal by the sequence shown as eq 1.[17] Precise mechanistic

$$\text{octanol} \xrightarrow{[O]} \text{octanal} \xrightarrow{[O]} \text{octanoic acid} \xrightarrow[-CO_2]{[O]} \text{heptanal} \quad (1)$$

details remain unknown, and the last step (photodecarboxylation) is quite inefficient, likely because of the inhibitory effect of CO₂ as solvent. It is likely the highly favorable thermodynamic driving force of this last step that makes it possible at all in this medium.

Since all photocatalytic reactions require preadsorption of reactant at the photocatalytically active site, the initial substrate is adsorbed near the active site and all subsequent oxidation intermediates are formed at or near the surface. The detection of heptanal therefore indicates that the surface hydrophobicity/solvation by supercritical CO₂ affects mass transport equilibria of partially oxidized intermediates to or from the surface.

Consistent with this sequence, as shown in Figure 6, the octanoic acid yield was optimal after about 2 h of irradiation,
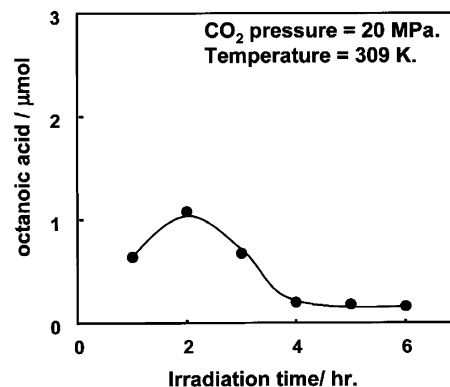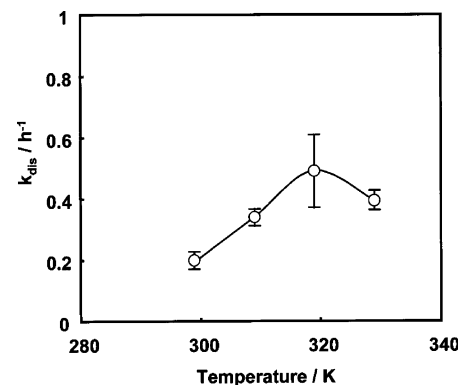
which corresponds with one half-life in the photocatalytic degradation of octanol in aerated scCO₂ at 20 MPa and 309 K under the stated reaction conditions. It is interesting that octanoic acid was most easily detected at high CO₂ densities, likely reflecting the difficulty in desorbing adsorbed octanoic acid from the TiO₂ surface.

Thus, alternate chemical routes for photocatalytic oxidation of organic compounds such as octanol in scCO₂ can be followed as a function of changes in CO₂ pressure. In addition, changes in CO₂ density effected by variations in pressure significantly influence observed selectivity, that is, the formation of octanal versus heptanal. Furthermore, these observations show that intermediate products that are formed during the photocatalytic oxidation and that are sometimes difficult to observe in photocatalysis on aerated TiO₂ in aqueous suspensions can be easily isolated and monitored by varying external pressure when the photocatalysis is conducted in scCO₂.

Effect of Temperature. Because an increase in temperature decreases near-surface CO₂ density, k_{dis} should be similarly influenced by changes in temperature at constant pressure. Figure 7 shows such a plot at constant pressure just above the critical point, 10 MPa. The observed k_{dis} increased with reaction temperature from 299 to 319 K as near-surface CO₂ density decreased, corresponding with the trend observed as CO₂ pressure was decreased (Figure 3). The k_{dis} at 329 K was almost the same as that at 319 K despite higher CO₂ density at the lower temperature. We believe that this experimental observation
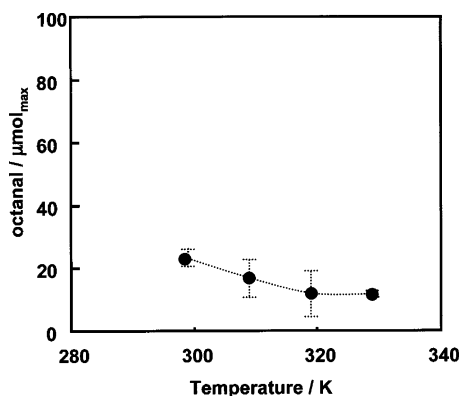
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Figure 8. Dependence on reaction temperature of the maximal photocatalytic production of octanal from *n*-octanol on irradiated silanized TiO_2 (T805) suspended in aerated $scCO_2$. CO_2 pressure: 10 MPa. Plotted values are absolute product yields observed in a 15-mL cell, reported as averages obtained from three experiments.
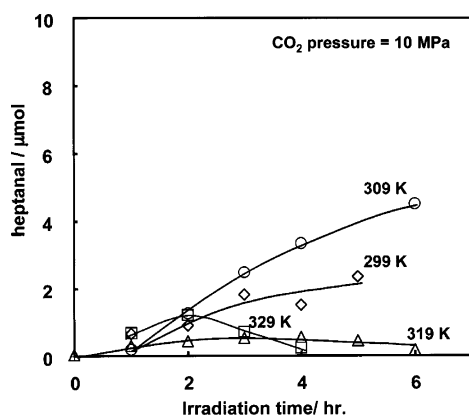

Figure 9. Photocatalyzed appearance of heptanal from *n*-octanol upon irradiation of silanized TiO_2 (T805) suspended in aerated $scCO_2$ as a function of irradiation time. CO_2 pressure: 10 MPa at 309 K. Plotted values are absolute yields produced in a 15-mL cell, reported as average data from three experiments.

reflects more efficient mass transfer of octanol from the photocatalytically active site as was described in a previous paper.[10]

Figure 8 shows the maximum yield of octanal produced as a function of the temperature. The efficiency of octanal production decreased upon raising the reaction temperature, presumably because of enhanced secondary oxidation as in eq 1.

Changes in the maximum yield of heptanal upon increasing temperature from 299 to 309 K are shown in Figure 9. At lowest temperature, CO_2 is a liquid, likely permitting only slow diffusion of heptanal from the surface of the photocatalyst. When the reaction temperature was increased from 309 to 329 K within the supercritical region, the concentration of heptanal decreased, possibly because of decreased mass transfer of heptanal upon decreasing $scCO_2$ density.

Thus, differences in CO_2 density caused by variations in temperature influence observed selectivity in the formation of octanal or heptanal. In addition, changes in reaction temperature produce the same effect as changes in CO_2 pressure in the supercritical region. Furthermore, changes in local density induced by temperature or pressure result in similar trends in product distribution.

Effect of Density on Photocatalytic Reactivity in scCO$_2$. If the observed photocatalytic reactivity of aerated T805 is controlled by CO_2 density, k_{dis} should roughly correlate with CO_2 density. To test this prediction, all data on k_{dis} and on
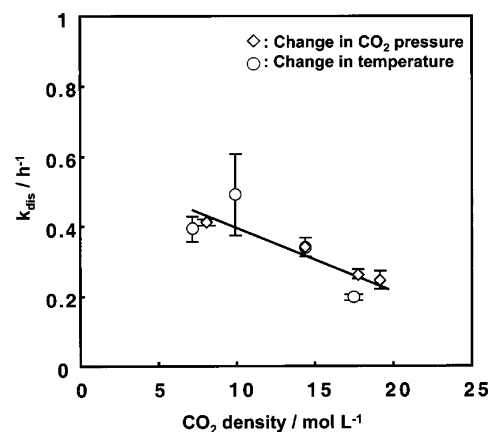

Figure 10. Dependence of k_{dis} on CO_2 density calculated for pure $scCO_2$ by the Peng–Robinson equation of state. Open diamonds and circles show apparent first-order rate constants obtained upon variation of CO_2 pressure and temperature, respectively.
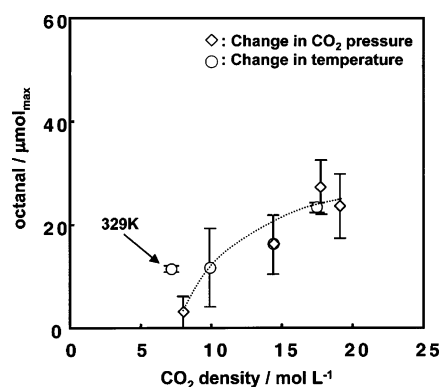

Figure 11. Comparison of calculated near-surface CO_2 density with the maximal production of initial oxidation product (octanal) from octanol on silanized TiO_2 (T805) in aerated $scCO_2$ (obtained from the Peng–Robinson equation of state). Open diamonds and circles show k_{dis} obtained upon variation of CO_2 pressure and reaction temperature, respectively. Plotted values are absolute yields produced in a 15-mL cell, reported as an average of three experiments.

product yield of octanal are replotted in Figures 10 and 11, respectively, together with the CO_2 densities calculated by the Peng–Robinson equation of state (Figure 1). In these figures, open diamonds indicate data for changes in pressure and circles illustrate changes in reaction temperature.

From Figure 10, k_{dis} decreased upon increasing CO_2 density in an apparently linear way. Thus, T805 photocatalytic activity is high at low CO_2 density, irrespective of whether the low density is achieved through variation of temperature or pressure, so long as the fluid remains supercritical.

Similarly, in Figure 11, data on the effect of reaction temperature and CO_2 pressure on the observed yield of octanal appear to follow the same trends. That is, octanal formed is efficiently desorbed from the surface of T805 as near-surface CO_2 density is increased. At a CO_2 density of 7.2 mol L^{-1} (at 329 K), octanal was easily detected, despite low CO_2 density, because of easy mass transfer from the photoactivated surface.[18]

Conclusions

Reaction temperature and pressure strongly affect the rate of photocatalytic oxidation of *n*-octanol on silanized TiO_2 (T805) suspended in aerated $scCO_2$ by controlling near-surface density of CO_2. As a result, yields of products formed at the active site of the photocatalyst will be significantly perturbed. The rate of photooxidative degradation increased as CO_2 pressure decreased

at constant temperature above the critical point. These experimental results are explained by differences in mass transfer efficiency of the reactants and products formed on partially desilanized T805 powder in aerated $scCO_2$.

Since the yields of octanal increased and heptanal decreased with an increase in CO_2 pressure at 309 K, improved selectivity for a specific intermediate oxidation product can be enhanced by adjusting pressure and temperature of photocatalysis in sc fluid. This reaction control is a highly desirable feature, which makes the mechanistic study of photocatalysis on metal oxides suspended in supercritical CO_2 a most interesting challenge.

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