Catalytic Oxidation of Toluene and Tetralin in Supercritical Carbon Dioxide

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The catalytic total oxidation of toluene and tetrahydronaphthalene (tetralin) in supercritical carbon dioxide over a 0.5% platinum γ-alumina catalyst was studied in a fixed-bed reactor. Toluene oxidation experiments were performed at 618, 633, 648 and 663 K, and at 7.93, 9.31 and 10.7 MPa. Tetralin oxidation experiments were performed at 573, 598, 623 and 648 K and at 8.96 and 10.0 MPa. Inlet concentrations of toluene and tetralin were varied in the ranges 569 to 2,858 ppm (mass/mass) and 1,420 to 3,648 ppm, respectively. Reactions were run at excess oxygen with a 25:1 molar ratio of oxygen to toluene and a 15:1 molar ratio of oxygen to tetralin. A stepwise mechanism was postulated for the oxidation reaction to describe the kinetics of toluene and tetralin oxidation in supercritical carbon dioxide, and the reaction orders and activation energies were determined.

Introduction

In recent years, supercritical CO_2 ($SCCO_2$) extraction of organic contaminants from water (Ghonasgi et al., 1991; Yeo and Akgerman, 1990; Roop and Akgerman, 1989a,b; Brignole et al., 1987) and soil (Erkey et al., 1992; Akgerman et al., 1992; Dooley et al., 1987; Brady et al., 1987; Capriel et al., 1986) has been evaluated as potential environmental remediation technologies. Supercritical extraction has an advantage over extraction by liquid solvents, since the extracted species can be separated from the supercritical fluid by simple pressure reduction. The fluid is then recompressed to supercritical conditions and recycled back to the extractor. Separation by pressure reduction, on the other hand, can be very difficult if the extracted phase crystallizes out of the supercritical phase, due to cooling on expansion, causing plugging of the expansion nozzle. In addition, recompression of the fluid back to the supercritical conditions is a major cost item associated with supercritical extraction. In case of extraction of contaminants from environmental matrices, the extracted species (the contaminants) are the nondesired compounds and they should be disposed of in an environmentally acceptable manner. One way to achieve extraction of organics from environmental matrices combined with destruction of the extracted species, is to combine supercritical extraction with on-line catalytic destruction. In such a hypothetical system, the stream from the extractor would be mixed with oxygen and fed to a catalytic reactor in which the organics will be oxidized. The reactor effluent will be recycled back to the extractor. The system will operate at constant pressure, hence eliminating the costly expansion/recompression step and will achieve destruction of contaminants. We have recently reported about the feasibility of a similar process where the extracted contaminants would be adsorbed on a suitable adsorbent (Madras et al., 1994a). The extraction/adsorption process would be effective when the contamination level of the matrix is low (typically less then 1,000 ppm) but becomes costly at high concentrations. We believe that the catalytic oxidation would be feasible at high initial concentration of organics in the environmental matrix. Data on oxidation of aromatics in supercritical carbon dioxide are needed to evaluate such a process.

$SCCO_2$ has been proved to be a feasible reaction medium under some reaction conditions. Hammond et al. (1985) investigated the catalytic activity of polyphenol oxidase in $SCCO_2$ at 309 K and 34.45 MPa, *p*-cresol and *p*-chlorophe-

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nol were readily oxidized to their corresponding *o*-benzoquinones. Conversions of 70–80% were achieved for oxidation of *p*-cresol, whereas the conversion for *p*-chlorophenol was 27%. Randolph et al. (1985) investigated the reaction of cholesterol to form cholest-4-en-one in $SCCO_2$ with cholesterol oxidase. A limitation of this work was the low solubility of the reactants and products in $SCCO_2$. They also performed a more detailed investigation of the same reaction in a flow reactor with a 9:1 CO_2/O_2 mixture (Randolph et al., 1988). These studies indicate that catalytic oxidation (enzymatic oxidation) in $SCCO_2$ is possible.

Recently, studies on catalytic partial oxidation of toluene in $SCCO_2$ over supported CoO catalyst (Dooley and Knopf, 1987) and complete oxidation of toluene and an aromatic-aliphatic hydrocarbon mixture in $SCCO_2$ over a Pt/Al_2O_3 catalyst (Pang et al., 1991) were reported. Pang et al. (1991) observed complete combustion at reaction temperatures over 523 K, but at lower temperatures partial oxidation products were detected. On CoO catalysts calcined and/or reduced at different conditions, and Dooley and Knopf (1987) reported apparent activation energies in the range of 5.1 to 38 kcal/mol. To the best of our knowledge, these are the only reported works on oxidation of organic pollutants in supercritical carbon dioxide.

Complete oxidation of organic contaminants in air has been widely studied. The mechanism and reaction rate expressions proposed can mainly be divided into three categories. The first one is the so-called Mars and van Krevelen mechanism (Golodets 1983), which assumes a reduction—reoxidation reaction on the catalyst surface. The first step of the mechanism is oxygen chemisorption (surface reoxidation) generating adsorbed atomic oxygen. The second step involves reaction of the organic compound in gas phase with an adsorbed oxygen, leading to the formation of reaction intermediates, which are then converted into reaction products, CO_2, and H_2O. The mechanism leads to a rate expression with first-order dependency of both oxygen and organic compound partial pressures. The second one is the Langmuir-Hinshelwood model (Patterson and Kemball, 1963; Klinghoffer and Rossin, 1992; Chang and Weng, 1993; Rossin and Farris 1993). Many investigators assume dissociative adsorption of oxygen and reaction with the adsorbed organic compound on the catalyst surface. Normally, it is assumed that the surface reaction between adsorbed oxygen and organic compound is the rate-controlling step. The assumptions result in a rate expression that is first-order in organic compound and one-half order in oxygen partial pressures. The third one is the power law model, which is an empirical rate expression and has been used by some researchers (Trimm and Irshad, 1970; Golodets 1983). In most of research work done on complete oxidation of organic compounds in air, a large amount of excess oxygen was used and the organic specie is the rate-limiting reactant. The molar ratio of oxygen to organic compounds is usually in excess of 100. This leads to the rate expressions that are functions of the organic specie's partial pressure only. Our objective is combining supercritical extraction with on-line oxidation to destruct the extracted hydrocarbons; therefore, in our studies we use a small amount of oxygen, preferably the stoichiometric amount, since, conceptually, the reactor effluent will be recycled back to the extractor. Therefore, in our case, we need to consider oxygen concentration dependency of the rate expression as well. Hence, the objective of this research was to study the oxidation kinetics of aromatic compounds (toluene and tetralin) over a 0.5% Pt/Al_2O_3 catalyst in $SCCO_2$ and to develop a rate expression model to predict the reaction rate over the experimental conditions.

Experimental

Toluene and tetralin (HPLC grade) were obtained from Sigma-Aldrich. CO_2 and O_2 were obtained from Bob Smith Corporation in Bryan, Texas, with a purity of 99.5%. The 0.5% $Pt/\gamma\text{-}Al_2O_3$ catalyst used in this study was obtained from Engelhard Corporation. The catalyst had a nominal BET surface area of 100 m^2/g. The spherical catalyst particles were crushed and particles with diameters in the range 100 to 200 μm were used in the reaction. Before the catalyst was placed into the reactor, it was pretreated by calcining in air. In the precalcining procedure, the oven temperature was increased from ambient to 723 K at a rate of 2 K per minute and held at 723 K for 16 h.

The schematic representation of the experimental assembly is presented in Figure 1. Liquid CO_2 was pumped through an ice bath by the liquid pump (LDC/Milton Roy, miniPump vs) at 273 K and 5.52 MPa and was mixed with toluene or tetralin delivered by a syringe pump (ISCO, LC-2600). The combined stream was mixed with a stream of high-pressure O_2, whose flow rate was controlled by a mass-flow controller (Brooks Instrument Division, 5850E). In order for the organic compound to be thoroughly mixed with O_2 and $SCCO_2$, the stream was passed over a 5-in-long column filled with 25/40-mesh glass beads. The inlet fluid was preheated up to the reaction temperature. It then passed through a half-inch tubular fixed-bed reactor containing the 0.5% PT/Al_2O_3 catalyst, which was diluted by same-size glass beads. The preheater and the fixed-bed reactor were placed in the same furnace whose temperature was controlled by a temperature controller (Omega, CN-350J) with ±1 K accuracy. The temperature of the reactor was monitored by a thermocouple that was placed in a thermowell inside the reactor. During operation, the temperature difference between the inlet and the outlet was less than 2 K. The system pressure was controlled by back-pressure regulator (Grove Valve and Regulator Corporation, S-91xw). The concentrations of toluene or tetralin and possible partial oxidation products in the reactor effluent were analyzed by on-line sample injection to a HP-5890 gas chromatograph equipped with a FID. O_2, CO_2, and CO, if produced, were checked by off-line sample injection into a CARLE Refinery GC equipped with a TCD. The feed concentration of toluene and tetralin were measured by on-line sample injection to the HP-5890 gas chromatograph through reactor by-pass line.

The fixed-bed reactor was operated in an integral mode. The reactor was filled with 0.005 to 0.035 g of catalyst, which was diluted to 4 cm^3 by 60/80-mesh glass beads. A total flow rate ranging from 3.69 to 8.83 mol/h was used with a 98:2 molar ratio of CO_2 to O_2, and a 25:1 molar ratio of O_2 to toluene in the toluene oxidation experiments when the inlet concentration of toluene was kept at a constant of 1,632 ppm (mass/mass), and a 15:1 molar ratio of O_2 to tetralin in the tetralin oxidation experiments. Further experiments were run

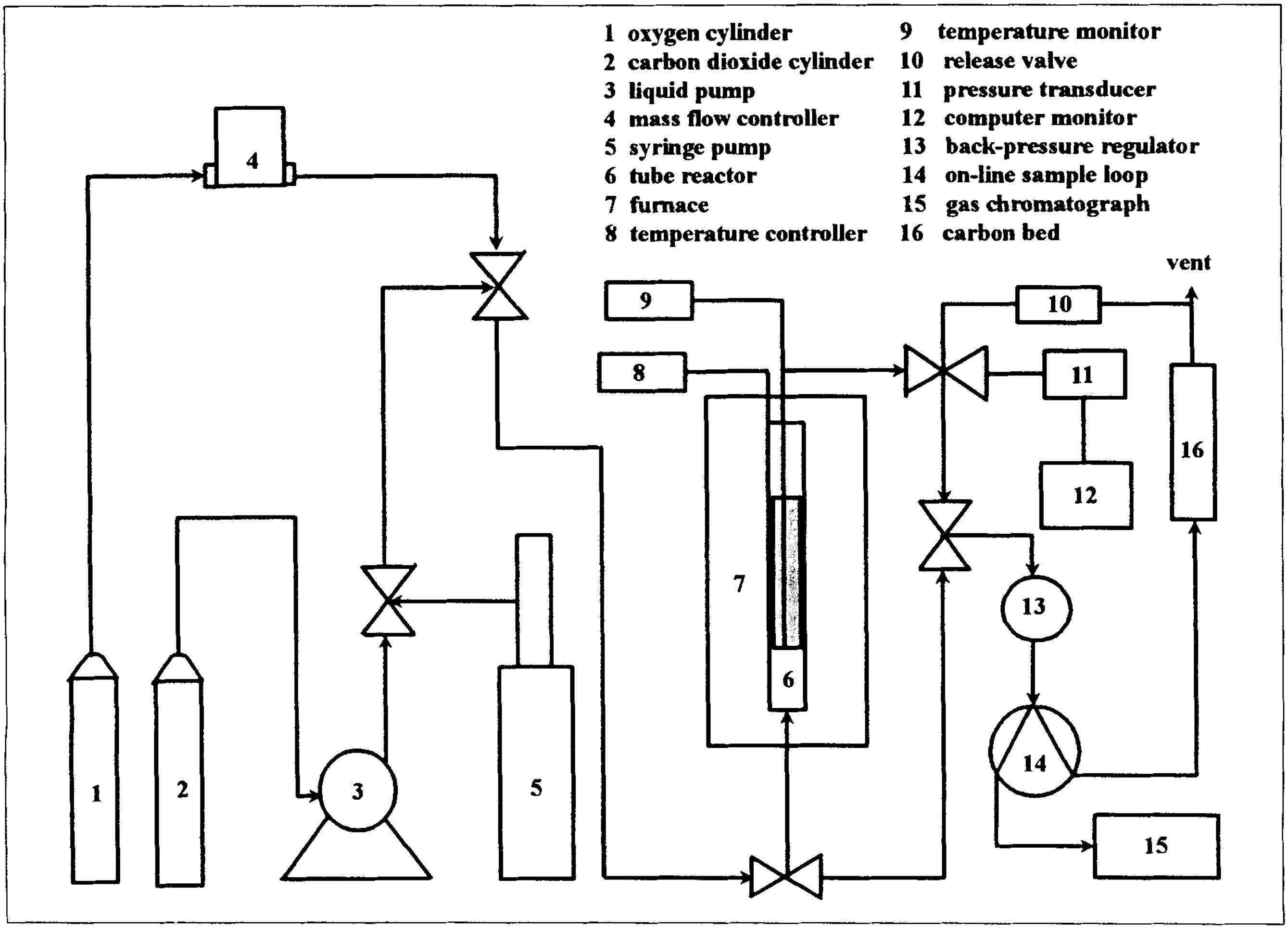

Figure 1. Experimental setup.

with the inlet concentration of toluene varying from 979 to 2,937 ppm, and the inlet concentration of tetralin varying from 1,420 to 3,648 ppm. The inlet concentrations of toluene and tetralin are in the typical concentration range of organic compounds in $SCCO_2$ after extraction. Toluene oxidation experiments were performed at 618, 633, 648 and 663 K, and at pressures of 7.93, 9.31 and 10.7 MPa. Tetralin oxidation experiments were performed at 573, 598, 623 and 648 K and at 8.96 and 10.0 MPa. The system pressures used in the experiments were in the typical pressure range of supercritical extraction by $SCCO_2$.

Results and Discussion

Catalyst activity and deactivation

In our preliminary studies, we observed that although there was significant catalyst activity at temperatures as low as 400 K, the catalyst deactivated rapidly at reaction temperatures of 423–523 K. The platinum on the catalyst surface formed a yellow-colored compound. Activity was restored completely when the catalyst was heated in $SCCO_2$ at temperatures above 548 K. We assumed that the deactivation was due to product inhibition (water reacting with Pt). At temperatures above 548 K, no deactivation was observed. Catalyst deactivation was measured at the lowest operating temperature for each oxidation reaction before running the experiments for kinetic studies. Figure 2 shows a time on stream analysis for toluene oxidation at 618 K and 9.31 MPa with an inlet toluene concentration of 1,632 ppm and space velocity (based on total flow rate) of 128 kmol/kg cat-h (WHSV 5,634 h^{-1}), and for tetralin oxidation at 573 K, 8.97 MPa, 2,259 ppm inlet concentration, and a space velocity of 39.7 kmol/kg cat-h (WHSV 1,746 h^{-1}). The absence of significant catalytic deactivation at these temperatures is consistent with the results reported by other researchers who studied the gas-phase oxidation of organic compounds over Pt/Al_2O_3 catalyst (Rossin and Farris, 1993; Klinghoffer and Rossin, 1992; Mendyka et al., 1992; Bond and Sadeghi, 1975).

Partial oxidation products

Many partial oxidation products can be produced by the oxidation of toluene and tetralin, depending on the reaction conditions. However, there were no by-products detected from the on-line and off-line samples. There was also no carbon monoxide produced after the reaction. The analytical results of the reactor effluent indicated that toluene and tetralin were completely oxidized. By-products could be detected only when the amount of O_2 introduced into the reac-

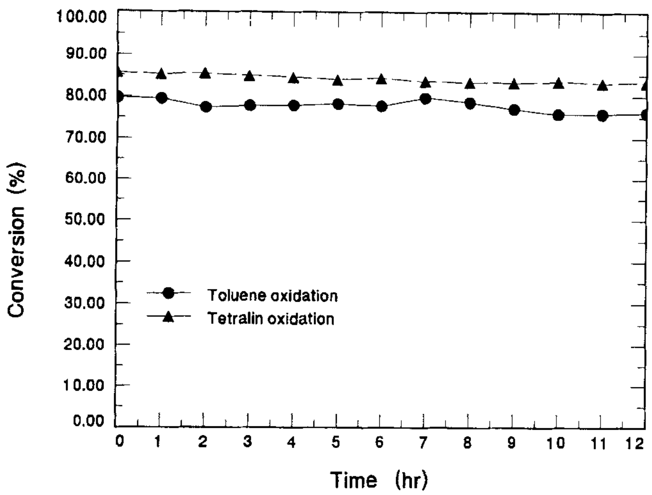

Figure 2. Time on stream analysis for catalyst activity.

Toluene at 618 K and 9.31 MPa and tetralin at 573 K and 8.97 MPa. Space velocities are 5,634 and 1,746 h^{-1}, respectively.

tor was less than the stoichiometric amount based on chemical reactions:

$$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O \tag{1}$$

$$C_{10}H_{12} + 13O_2 \rightarrow 10CO_2 + 6H_2O \tag{2}$$

Reaction conversions

Figure 3 shows the conversion of toluene vs. space–time at four different temperatures. The system pressure during the experiments was 9.31 MPa, which is within the pressure range usually used in supercritical extraction of organic compounds from soil or water by $SCCO_2$. The total flow rate of the reaction mixture was kept at 5.05 mol/h, and the mole fractions of O_2 and toluene in the feed stream remained unchanged during the experiments. The inlet concentration of toluene was 1,632 ppm, and molar ratio of O_2 to toluene was 25:1. Space velocity was varied by changing the amount of catalyst placed in the fixed-bed reactor. Tetralin conversion data are plotted in Figure 4. The reactions were conducted at 8.96 MPa and at temperatures of 573 K to 648 K. The mole fraction of O_2 and tetralin in the feed stream was kept constant. O_2 to tetralin molar ratio was 15:1 for the experiments at the four different temperatures. The inlet concentration of tetralin was 2,259 ppm. Space–time was varied either by changing the amount of catalyst in the reactor or by changing the total flow rate of the mixture, which varied from 3.68 mol/h to 8.83 mol/h.

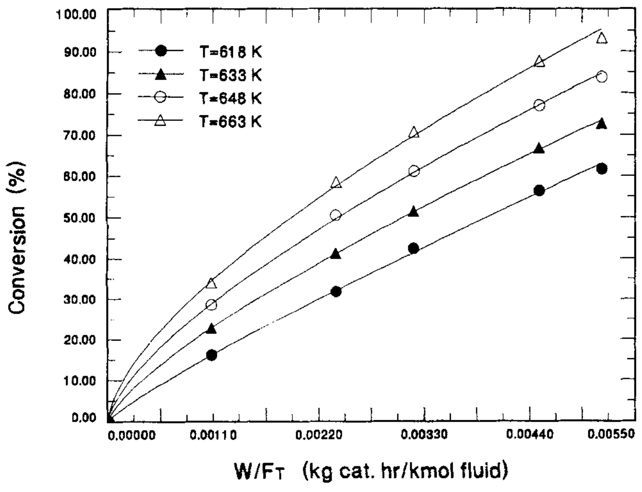

Figure 3. Toluene conversion to total oxidation products at 9.31 MPa.

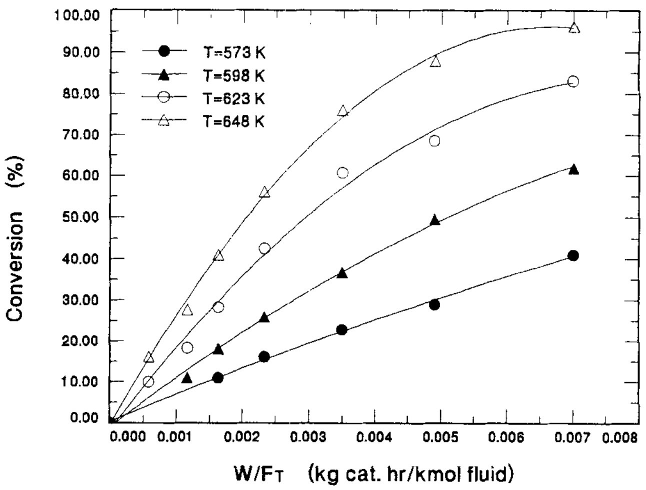

Figure 4. Tetralin conversion to total oxidation products at 8.97 MPa.

Analysis of external and internal diffusion resistances

External mass-transfer coefficients are usually expressed in the form of the Sherwood number and are correlated as a function of the Schmidt and Reynolds numbers. Wakao and Kaguei's correlation predicts mass-transfer coefficients for a wide range of Reynolds and Schmidt numbers (Wakao and Kaguei, 1982).

$$Sh = 2 + 1.1 Sc^{1/3} Re^{0.6} \tag{3}$$

Recently, this correlation has been used to predict the overall mass-transfer coefficients in supercritical fluids (Madras et al., 1994b). Internal mass-transfer is controlled by effective pore diffusivity in the particles pores, and the following well-known expression has been recommended for predicting effective pore diffusivity in supercritical fluids as well (Madras et al., 1994b):

$$D_e = \frac{\epsilon_p}{\tau_p} D_m, \tag{4}$$

where D_m is the diffusion coefficient of the organic compound in the supercritical fluid, ϵ_p is the particle porosity, and τ_p is the tortuosity factor. A reasonable approximation can be assumed as $\tau_p = 1/\epsilon_p$. The general criterion for the absence of internal diffusion limitation is (Froment and Bischoff 1979)

$$\Phi = \frac{\dfrac{(r_A \rho_s)_{\text{obs}} L^2 f(C_s^s)}{C_s^s}}{2 \displaystyle\int_{C_{s,\text{eq}}}^{C_s^s} D_e(C) f(C) dC} \ll 1. \tag{5}$$

Assuming that D_e is constant and $C_{s,eq} = C_s^s(1-x_e)$, and taking $f(c) = C_A^{\alpha} C_B^{\beta}$, then Eq. 3 becomes

$$\Phi = \frac{(r_A \rho_s)_{\text{obs}} L^2}{2 D_e C_s^s \displaystyle\int_0^{x_e} (1-x)^{\alpha} (1-9\gamma x)^{\beta} dx} \ll 1. \tag{6}$$

for the reaction, and γ is the ratio of C_{sA}^s to C_{sB}^s.

To calculate the external mass-transfer coefficient and internal effective pore diffusivity, the data on molecular diffusivities must be known. Although the reaction stream contains O_2, CO_2, and toluene or tetralin, the stream is mainly $SCCO_2$ and the concentrations of O_2 and organic compounds are very low. Hence, the mixtures are considered a pseudobinary system, including CO_2 and organic compound. The Chapman and Enskog equation for diffusion in dense fluids was used to estimate the molecular diffusivities of organic compounds in CO_2. Molecular diffusivities in supercritical fluids can be predicted by scaling the low-pressure diffusion coefficient (Chapman and Cowling, 1970). For the system of CO_2 and toluene, the predicted molecular diffusivities are 2.451×10^{-3} cm^2/s at 618 K and 9.31 MPa, and 2.811×10^{-3} cm^2/s at 663 K and 9.31 MPa. For CO_2/tetralin system, the diffusivities are 1.741×10^{-3}cm^2/s 573 K and 8.97 MPa, and 2.221×10^{-3} cm^2/s at 648 K and 8.97 MPa. The effective diffusion coefficients were calculated by taking $\epsilon_p = 0.56$, as measured in our laboratories. Under any operation conditions of the oxidation experiment, $k_g d_p / D_e$ is always greater than 10, so the external mass-transfer resistances are not important. The internal diffusion limitation was evaluated by substituting the data into Eq. 6. The values of Φ were obtained as $\Phi = 0.17$ at 618 K and $\Phi = 0.19$ at 663 K for toluene oxidation, and $\Phi = 0.12$ at 573 K and $\Phi = 0.27$ at 648 K for tetralin oxidation. Considering the uncertainty involved in estimated parameters, these values do not satisfy the criterion set by Eq. 6 with sufficient degree of confidence. Therefore we used two different catalyst sizes, 100–200 μm and 75–100 μm, to determine whether the internal diffusion effects are negligible. Toluene conversion data were taken using these catalysts. The conversion data at different temperatures employing both catalysts are shown in Figure 5. The experiments were operated at the inlet toluene concentration of 1,632 ppm, 25:1 molar ratio of O_2 to toluene, and the space-time of 3.05 kg cat·h/kmol toluene for both catalysts. The experimental results presented in Figure 5, combined with the general criterion given by Eq. 5, indicate that internal diffusion limitation is negligible.

Mechanism of the toluene and tetralin oxidation and parameter estimation

For a plug flow, isothermal, integral fixed-bed reactor that is operated in the absence of internal and external mass-transfer resistance, the design equation is (Froment and Bischoff 1979)

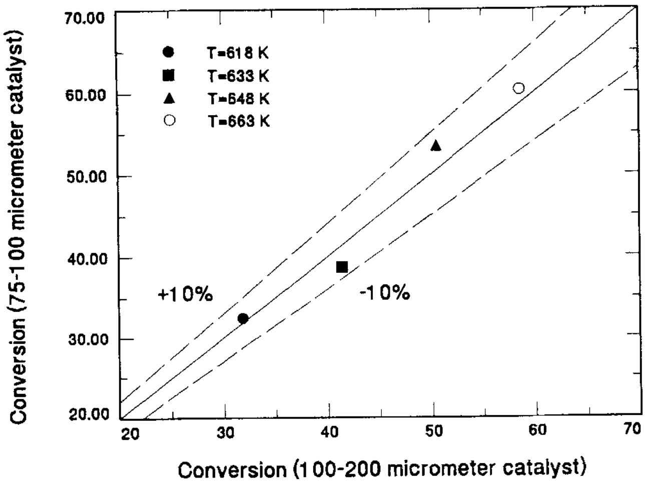

Figure 5. Experimental verification of negligible internal diffusion effects.

$$\frac{W}{F_{A0}} = \int_0^x \frac{dx_A}{r_A} \tag{7}$$

where x is the reaction conversion, and r_A is the rate expression for component A. Different kinds of rate expressions, such as the Mars and van Krevelen model (Golodets, 1983) and the Langmuir–Hinshelwood model (Patterson and Kemball, 1963; Klinghoffer and Rossin, 1992; Chang and Weng, 1993; Rossin and Farris, 1993) were evaluated during the study. Standard statistical tests indicated that these rate expressions did not fit the experimental data. Further regression analysis showed that the best fitting rate expression is one with a half order dependence on oxygen partial pressure and a fractional order dependence on toluene and tetralin partial pressures, indicating dissociative adsorption of both oxygen and the organic compounds. Therefore, a stepwise Langmuir–Hinshelwood-type oxidation mechanism is assumed here to model complete oxidation of toluene and tetralin.

It is assumed that both O_2 and the organic compounds are dissociatively adsorbed on the catalyst surface. Dissociative adsorption of oxygen reaction has been widely reported (Satterfield, 1980; Golodets, 1983; Chang et al., 1992; Chang and Weng, 1993), and scission of carbon–carbon bond on noble metal catalyst surface has been postulated in some reactions (Yagasaki and Masel, 1990; Brucker and Rhodin, 1977; Barteau et al., 1984; Kohler et al., 1987). Therefore, the mechanism of oxidation reaction can be expressed as follows:

$$O_2 + 2S \rightleftharpoons 2OS \tag{1'}$$

$$R_m + nS \rightleftharpoons R_{m1}S + R_{m2}S + \ldots \tag{2'}$$

$$CO_2 + S \rightleftharpoons CO_2S \tag{3'}$$

$$R_{m_i}S + OS \rightarrow R_{m_i}OS + S \tag{4'}$$

$$R_{m_i}OS + OS \rightarrow R_{m_i}O_2S + S \tag{5'}$$

$$R_{m_i}O_2S + OS \rightarrow (R_{m_i} - H)O_2S + HOS \tag{6'}$$

$$HOS + (R_{m_i} - H)O_2S \rightarrow H_2OS + (R_{m_i} - 2H)O_2S \tag{7'}$$

or

$$R_{m_i}O_2S + OS \rightarrow (R_{m_i} - C)OS + CO_2S \qquad (8')$$

$$CH_2OS + OS \rightarrow CH_2O_2S + S \qquad (n'-2)$$

$$CH_2O_2S + OS \rightarrow CO_2S + H_2OS \qquad (n'-1)$$

$$H_2OS \rightleftharpoons H_2O + S \qquad (n')$$

It is assumed that the reaction (4′) is the rate-controlling step with reactions (1′), (2′), (3′), and (n') in dynamic equilibrium, and reactions through (5′) to ($n'-1$) occurring very fast and being kinetically not significant. It is further postulated that reaction (4′) is irreversible. Based on these assumptions, the following rate expression is obtained:

$$r = \frac{dC_{R_m}}{dt} = \frac{k_{4'}C_{t'}^2(K_{1'}C_{O_2})^{1/2}(K_{2'}C_{R_m})^{1/n}}{\left[1 + (K_{1'}C_{O_2})^{1/2} + n(K_{2'}C_{R_m})^{1/n} + K_{3'}C_{CO_2} + K_{n'}C_{H_2O}\right]^2}, \qquad (11)$$

where n is the number of sites in reaction (2′), adsorption of the organic compound on the surface on n sites with carbon–carbon bond scission. At the experimental conditions, the concentrations of oxygen, organic compounds, and water are very small since the system is 98+% CO_2. If the constant $K_{1'}$, $K_{2'}$, and $K_{n'}$ are not very large, the rate expressions can be reduced into

$$r = \frac{dC_{R_m}}{dt} = k_4'(C_{O_2})^{1/2}(C_{R_m})^{1/n} \qquad (12)$$

with

$$k_4' = \frac{k_{4'}C_t^2 K_{1'}^{1/2} K_{2'}^{1/n}}{[1 + K_{3'}C_{CO_2}]^2}. \qquad (13)$$

Considering the reactions at different temperatures, the preceding exponential rate expression can be rewritten as

$$r_A = A_0 \exp\left(-\frac{E_a}{RT}\right)(C_A)^{1/n}(C_{O_2})^{1/2}. \qquad (14)$$

Here, C_A represents the concentration of the reactant toluene or tetralin, C_{O_2} is the concentration of O_2, A_0 is the frequency factor, and E_a is the apparent activation energy of the reaction including the temperature dependency of the rate constant k_4 and the adsorption equilibrium constants $K_{i'}$. Because the system is 98% CO_2, it is reasonable to assume constant overall density at constant temperature and pressure. Therefore, the molar volume of the mixture was assumed constant to calculate molar concentrations. Kinetic parameters were obtained by fitting the experimental data with the correlation in the integral form of Eq. 7 using a nonlinear least-squares algorithm that minimized the sum of the error between the predicted and the experimental values of W/F_{A0}:

$$f = \sum \left[\left(\frac{W}{F_{A0}}\right)_{\text{pred}} - \left(\frac{W}{F_{A0}}\right)_{\text{exp}}\right]^2. \qquad (15)$$

Reaction orders of toluene or tetralin and activation energy were determined for toluene and tetralin oxidation by fitting the conversion data at different space–times and the four different temperatures given in Figures 3 and 4.

The form of the rate expression that gave the best fit for the experimental toluene conversion data was the one with $n = 1.96$ and an activation energy of 14.42 kcal/mol:

$$r_A = (2.259 \pm 0.214) \times 10^6 \exp\left(-\frac{14{,}420 \pm 1{,}547}{RT}\right) \times C_A^{0.51 \pm 0.09} C_{O_2}^{0.5}. \qquad (16)$$

The tetralin oxidation data were also fitted to Eq. 11, resulting in the rate expression

$$r_A = (2.436 \pm 0.317) \times 10^7 \exp\left(-\frac{17{,}166 \pm 2{,}253}{RT}\right) \times C_A^{0.46 \pm 0.08} C_{O_2}^{0.5}. \qquad (17)$$

Here, the order of 0.46 for tetralin implies $n = 2.17$ in Eq. 14. Activation energy of the preceding reaction is 17.17 kcal/mol. The value of the activation energy for toluene obtained in this research was lower than the values reported by Yao (1984), in the range 21 to 29 kcal/mol for gas-phase oxidation of toluene over Pt/Al_2O_3 at low pressures. Yao states that the activation energy for oxidation of toluene changed with the change of platinum concentration in the catalyst and the catalyst calcination conditions. Two reasons could be attributed to the lower activation energy we observe for oxidation of toluene compared to Yao's work. The first one is that the catalyst used in this study had different platinum content and was calcined at different conditions. The second one is the adsorption of CO_2 on the catalyst surface. On the other hand, there are many studies on gas-phase complete oxidation of aromatic compounds on supported platinum catalysts and activation energies ranging from 5.02 kcal/mol to 29 kcal/mol reported in the literature (Barresi et al., 1992; Frost et al., 1991; Gangwal et al., 1988; Hubbard et al., 1993; Otto et al., 1991; Schartz et al., 1971; Yao, 1984, 1980). In addition, Larsson and Jonson (1989) studied toluene oxidation on titania-supported vanadium catalysts and showed that the apparent activation energy was affected by the reactants' heat of adsorption on the catalyst surface as well as the amount of vanadium. They reported values in the range 13.2 to 34.4 kcal/mol.

The reaction orders are 0.51 for toluene and 0.46 for tetralin. Since these values are very close to 0.5, it may be concluded, at least for toluene and tetralin, that these compounds dissociate into two parts during the oxidation reaction in $SCCO_2$ with $n = 2$ in the oxidation mechanism.

In order to evaluate the validity of the rate expressions

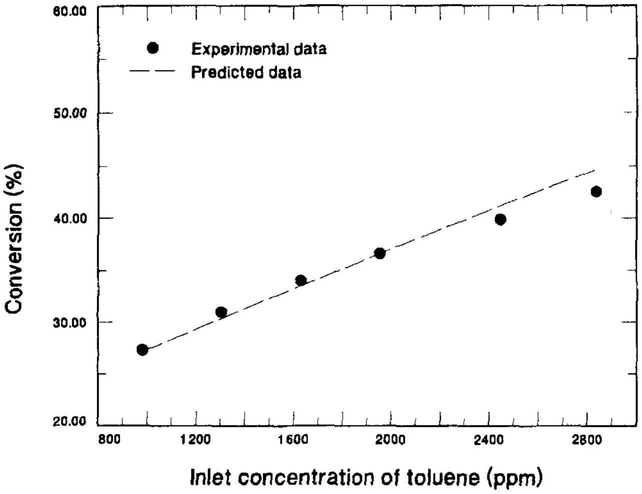

Figure 6. Variation of toluene conversion with inlet concentration and the model prediction at constant space velocity and oxygen concentration and at 9.31 MPa and 618 K.

given by Eqs. 16 and 17, we have taken data at different inlet conditions and at different pressures and attempted to predict the data with the same rate expressions with no adjustments of the parameters. Figure 6 shows the experimental data and prediction for oxidation of toluene where the inlet concentrations of toluene were changed. In the experiment, we kept the constant space-time (3.05 kg cat.·h/kmol) and concentration of oxygen (0.03641 mol/L), but varied the inlet concentration of toluene in the range 979 to 2,937 ppm at the operating temperature of 613 K and the pressure of 9.31 MPa. With tetralin, we kept the tetralin flow rate constant (constant space-time of 9.47 kg cat.·h/kmol), but varied the flow rate of $SCCO_2$ resulting in a concentration range of 1,420 to 3,648 ppm at the operating temperature of 573 K and the pressure of 8.96 MPa. The experimental and predicted data at different inlet concentrations of tetralin is shown in Figure 7.

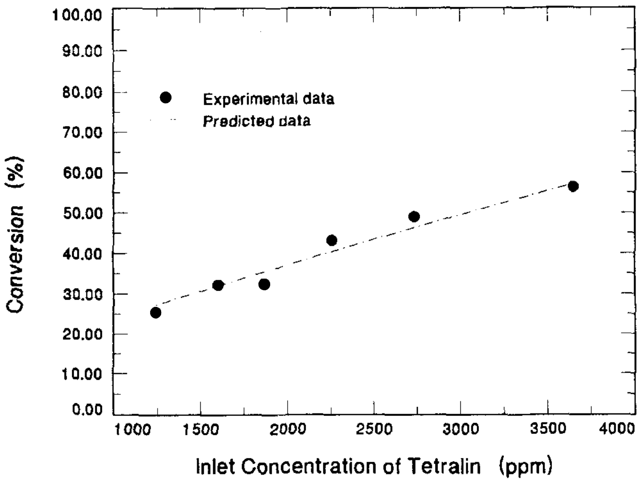

Figure 7. Variation of tetralin conversion with inlet concentration and the model prediction at 8.97 MPa and 573 K.

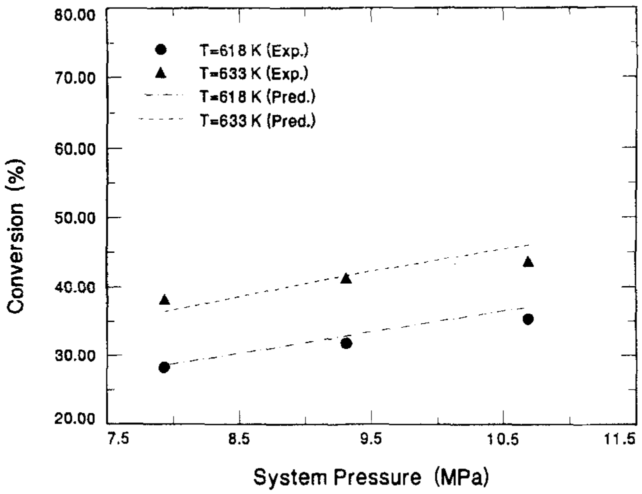

Figure 8. Pressure effect on toluene conversion and the model prediction.

Pressure effect on the reaction rate is an important phenomenon in reactions in supercritical fluids (Paulaitis and Alexander, 1987). Figure 8 shows the effect of pressure on the reaction on the reaction conversion. Three pressures at two different temperatures were used in the experiments. The space-time in the toluene oxidation experiments was 3.05 (kg cat.·h/kmol toluene), and the inlet concentration of toluene was 1,632 ppm. The increase in conversion due to pressure is misleading, however, since the molar density of the stream increases with pressure, resulting in higher concentrations for the hydrocarbon and oxygen, although the mole fractions remain the same. Predictions by Eq. 16 are also demonstrated in Figure 9. The prediction has a very good agreement with the experimental data. This demonstrates that the pressure has little or no effect on the reaction rate constant within the operating pressure range. Figures 9 and 10 are the parity plots for toluene and tetralin oxidation, including all the experimental data and predictions by Eqs. 16 and 17. The standard deviations between the predicted and experimental values of

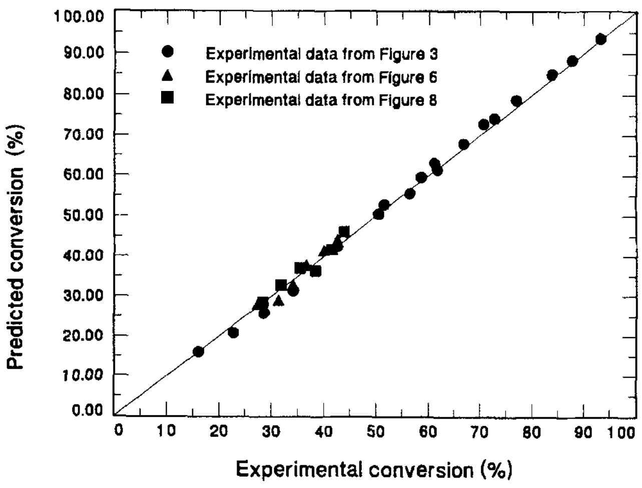

Figure 9. Parity for toluene oxidation.

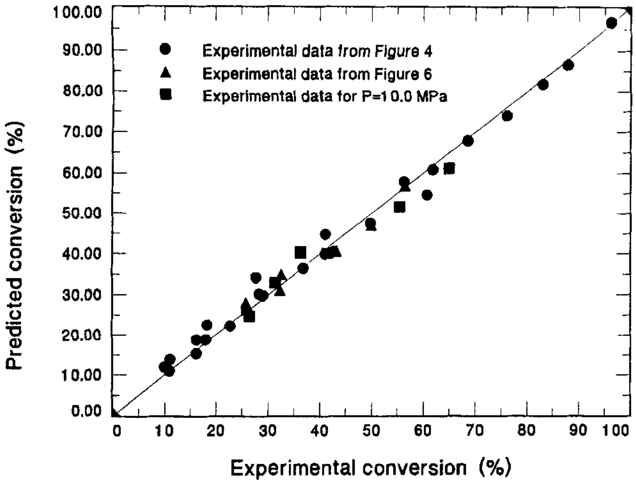

Figure 10. Parity for tetralin oxidation.

W/F_{A0} were less than 4%. Both figures show that the rate expressions accurately predict the experimental conversion data.

Conclusion

Total oxidation of toluene and tetralin in $SCCO_2$ into CO_2 and water has been achieved over a 0.5% Pt/Al_2O_3 catalyst at moderate temperatures (573 to 663 K) and pressures (7.93 to 10.7 MPa). It is shown that the reaction kinetics can be expressed in terms of dissociative adsorption of oxygen and hydrocarbon and a stepwise oxidation mechanism with surface reaction control. The rate expressions regressed from the experimental data predict data at different operating conditions as well. Further studies showed that the pressure has little effect on the reaction rate constant over the pressure range used in these experiments.

Acknowledgments

This project has been funded by grant 112TAM0310 in part with Federal Funds as part of the program of the Gulf Coast Hazardous Substance Research Center, which is supported under cooperative agreement R815197 with the U.S. Environmental Protection Agency and in part with funds from the state of Texas as part of the program of the Texas Hazardous Waste Research Center. The contents do not necessarily reflect the views and policies of the U.S. EPA or the state of Texas nor does the mention of trade names or commercial product constitute endorsement or recommendation for use.

Notation

d_p = particle diameter, m
D_e = effective pore diffusion coefficient, m^2/s
f = concentration distribution function; function of the sum of predicted and experimental data of space-time
F_{A0} = molar flow rate of the reactants, kmol/h
F_T = molar flow rate of total fluids, kmol/h
k_g = mass-transfer coefficient between particles and supercritical fluids, m/s
L = equivalent length of the catalyst, m
P = pressure, Pa
R = gas constant, cal/(mol·K)
t = time, s
T = temperature, K
W = weight of catalyst, kg
$\alpha\beta$ = reaction order, dimensionless
μ = fluid viscosity, N s/m^2
ρ = fluid density, kg/m^3

Subscripts

B = component
R_m = hydrocarbon
s = surface of the particle

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Manuscript received Dec. 28, 1993, and revision received Oct. 7, 1994.