Acceleration of Chlorination of Alumina Using Supercritical CCl_4

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In the Alcoa smelting process, anhydrous aluminum chloride is electrolytically converted to aluminum metal. This process could have a major impact on the aluminum industry if an efficient way of making the anhydrous aluminum chloride from alumina were found (Othmer et al., 1978). To make aluminum chloride, carbon and chlorine must be added to alumina. The carbon and chlorine reactants can take many forms, but carbon tetrachloride is convenient in that the carbon and chlorine are together in a single molecule. The net reaction is written as:

$$2\,Al_2O_3(s) + 3\,CCl_4(g) \rightarrow 4\,AlCl_3(g) + 3\,CO_2(g) \quad (1)$$

The kinetics of this reaction have received considerable attention but the rates of the reaction have been too slow to justify industrial development.

In this study, means of increasing the reaction rate by operating at supercritical conditions are experimentally investigated. The reaction product, $AlCl_3$, is soluble in the supercritical reactant, and the solubility enhancement that supercritical fluids display is a reasonable explanation for the increases in the observed rate, which are reported.

Experimental Procedure

Alumina, 5–10 g, solid, and excess carbon tetrachloride, 30–60 g, liquid, were combined in a batch reactor and heated rapidly to reaction conditions. Pressures of 4 to 10 MPa and temperatures of 563 to 643 K were supercritical with respect to carbon tetrachloride (T_c = 283°C, P_c = 4.5 MPa) and were monitored continuously. Conversions were determined by extracting the reaction products with water and measuring the amount of unconverted alumina. Alumina is the only water-insoluble solid in the reactor. At the conditions studied, particle size (mass average dia. 60 μm, number average dia. 6 μm N_2 BET surface area 60 m^2/g) and the total mass of alumina charged had no effect on the reaction rate per unit mass and hence fluid-solid mass transfer is considered to be unimportant in the overall reaction rate process. Runs with smaller particles produced no increase in the reaction rate, which indicates that internal mass transfer limitations are not important.

Reaction rates were measured by dividing the amount of alumina converted by the isothermal reaction time. A correction was made for the conversion during the heat-up period using the measured activation energy. This correction was verified experimentally by stopping several runs as soon as run temperature was reached. These runs yielded 1 to 5% conversion during heat-up. Conversions ranged from 6 to 48% except for one high-temperature run where the conversion reached 73%. In addition, the assumption of irreversibility of the reaction for these conversions was verified by two runs showing very high conversion (88%) as run time was lengthened to 4 h.

Results and Discussion

The results obtained in this study are summarized in Figure 1, which also shows, under noncritical conditions, the results of previous investigators (Bertoti et al., 1980, 1982; Pap and Bertoti, 1984; Pap et al., 1984). The primary difference between the present results and those of previous investigators is that the present experiments were conducted at much higher pressures (densities) and lower temperatures. The results indicate that while the activation energy obtained in this study (194 kJ/mol) is comparable to that obtained in the earlier studies (209–212 kJ/mol), the reaction rates obtained are several orders of mag-

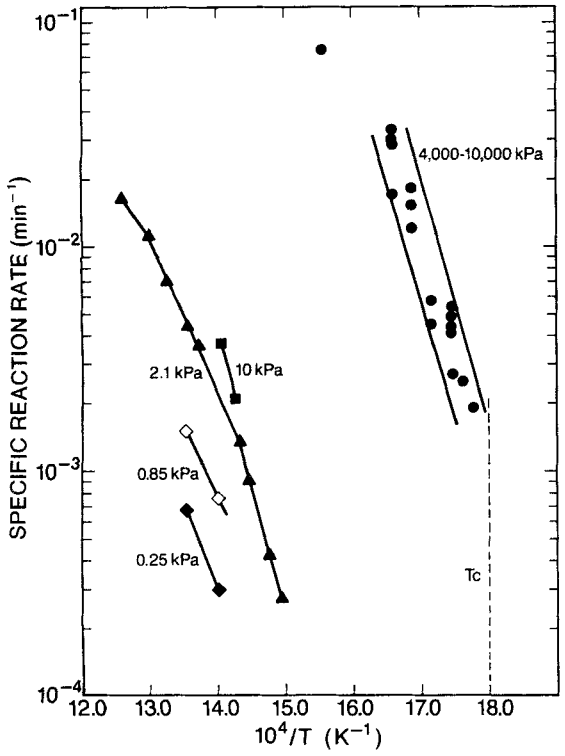

Figure 1. Experimental specific reaction rates at various pressures.

nitude higher than the earlier studies would have predicted, even after correcting for the pressure dependence of the earlier reactions.

The reaction involves several steps (Bertoti et al., 1982):

Adsorption of carbon tetrachloride onto the alumina

Surface reactions, which involve the formation of carbonyl chloride, carbon dioxide, aluminum trichloride, and dialuminum hexachloride

Desorption of reaction products

Some of the desorption takes place before the reactions are complete. For example, the carbonyl chloride can react on the surface of form aluminum chloride and carbon dioxide, or it can desorb from the surface.

The major difference between the present and earlier studies is the density of the carbon tetrachloride; it is supercritical in the present study (0.4 to 0.8 g/cm^3). A supercritical fluid phase is unlikely to have a large effect on the reaction rate (Eckert, 1972), since all reactions take place on a solid surface. However, a supercritical fluid can dramatically increase the solubility of the reaction products and can increase the rate of desorption from the surface.

From the lack of particle size effect and from the high activation energy, it is clear that both the high-temperature/low-pressure and high-pressure (density)/low-temperature results are chemically controlled. Bertoti et al. (1980) reported that the process was chemically controlled up to 547°C, so the higher rates obtained in the present study are most likely due to a change in a chemically controlled rate-limiting step.

In their nonisothermal thermogravimetric analysis runs, Bertoti et al. (1982) identified a physical adsorption step in which alumina samples gained weight due to adsorption of carbon tetrachloride at room temperature. Upon further heating, the carbon tetrachloride slowly desorbed until a temperature of about 150°C was reached, when chemical adsorption with substitution of chlorine for oxygen took place. At a temperature of 380°C rapid vaporization of the reaction products took place. In the isothermal runs used to obtain their kinetic data, the same steps took place. If desorption of the chemisorbed products was the rate-limiting step, then the phenomena observed in the present study can be attributed to enhanced desorption of the products, which allows renewal of the surface for further reaction. In this interpretation, the enhanced desorption is due to the greater solubility of the products in the supercritical phase and the rate has been shifted from a desorption-limited to a reaction-limited regime by the surface rate.

Model

If the mechanism consists of a reversible adsorption followed by irreversible reaction and desorption, the following sequence of steps can be written:

$$C + S \rightleftharpoons C \cdot S \tag{1}$$

$$C \cdot S \rightarrow A \cdot S \tag{2}$$

$$A \cdot S \rightarrow A_{(g)} + S \tag{3}$$

where C represents carbon tetrachloride, S represents the alumina surface site, and A represents aluminum chloride. The first step is considered to be at equilibrium so

$$C_C C_v = K_C C_{C\cdot S} \tag{4}$$

The gas phase concentration, C_C, is proportional to P_C/Z where P_C is the carbon tetrachloride pressure and Z is the compressibility factor. Thus:

$$P_C C_v = Z K_C C_{C\cdot S} \tag{5}$$

For the irreversible steps 2 and 3 the rates, r, must be equal and can be written as:

$$-r = k_1 C_{C\cdot S} = k_2 C_{A\cdot S} \tag{6}$$

where the stoichiometry is included in the rate constants. The total number of surface sites is composed of vacant sites C_v, sites with adsorbed reactant $C_{C\cdot S}$, and sites with adsorbed product $C_{A\cdot S}$. Thus:

$$C_S = C_v + C_{C\cdot S} + C_{A\cdot S} \tag{7}$$

or

$$\begin{aligned} C_v &= C_S - C_{C\cdot S} - C_{A\cdot S} \\ &= C_S - C_{C\cdot S} - k_1/k_2 C_{C\cdot S} \\ &= C_S - (1 + k') C_{C\cdot S} \end{aligned} \tag{8}$$

Combining Eqs. 5, 6, and 8 gives

$$-r = \frac{k_1 C_S P_C}{Z K_C + (1 + k') P_C} \tag{9}$$

where k' is the ratio of the surface rate to the desorption rate.

The solubility of a substance in a supercritical fluid is normally exponentially proportional to the fluid density (McHugh and Krukonis, 1986), which is in turn proportional to P/Z. Assuming that the desorption rate is proportional to the solubility of A (aluminum chloride) in the supercritical fluid we can write

$$k' = \frac{k_1}{k_2} = \frac{\text{surface rate}}{\text{desorption rate}} = \frac{k_1}{k_{2,0}e^{+\alpha P/Z}} = ke^{-\alpha P/Z} \quad (10)$$

where α is an empirical model parameter. The overall rate is thus

$$-r = \frac{k_1 P_C}{ZK_C + (1 + ke^{-\alpha P/Z})P_C} \quad (11)$$

At low pressures where $Z \sim 1$ and $P \sim 0$, the model reduces to:

$$-r = \frac{k_1 P_c}{K_C + (1 + k)P_c} \quad (12)$$

at high pressures $e^{-\alpha P/Z} \sim 0$

$$r = \frac{k_1' P_c}{ZK_C + P_c} \quad (13)$$

or

$$r = \frac{k_1'(P_C/Z)}{K_C + (P_C/Z)} \quad (14)$$

at very high pressures P_C/Z becomes nearly constant for any fluid so that the rate should approach a constant. The enhancement, E, in the reaction rate due to supercritical densities is given by

$$E = \frac{1 + k}{1 + K_C\left(\frac{P_C}{Z}\right)^{-1}_{\text{limiting}}} \quad (15)$$

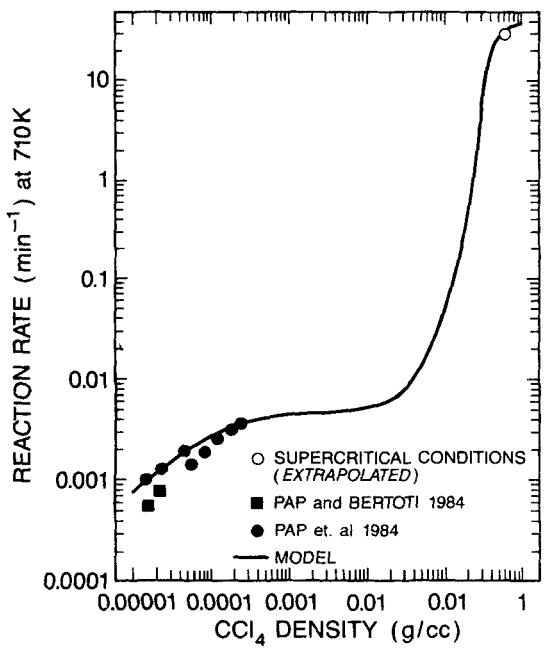

Figure 2. Comparison of model and experimental rates at 710 K.

The supercritical (O) is extrapolated over temperature at constant density using the data of Figure 1

Figure 2 shows how the proposed model fits the experimental data. In this figure, the high-density data (0.6 g/cm^3) have been extrapolated to 710 K using an activation energy of 194 kJ/mol. The model parameters used are K_C = 61,000 kPa, k = 26,600, k_1' = 111 min^{-1}, and α = 0.000588 kPa^{-1}. The density is obtained from $\rho = MP/(ZRT)$ and the compressibility factor Z is obtained from the Peng-Robinson (1976) equation of state. This simple model fits both the high- and low-density data quite well.

Conclusions

This study presents an example where supercritical fluids can dramatically increase the rate of a chemical reaction due to the properties of the supercritical fluids. The rate is enhanced by removing an adsorbed product that is limiting the surface area available for reaction. Supercritical fluids could produce similar effects in other reactions by selectively removing reaction products or inhibitors from an adjacent phase, solid or liquid, where the reaction is taking place.

Notation

A = aluminum chloride
C = carbon tetrachloride
C_i = concentration of species i
g = gas phase
k = ratio of surface reaction rate to desorption rate at zero pressure
k' = k at pressure P
k_1 = surface-specific reaction rate constant, g · min^{-1}/surface CCl_4
k_1' = $k_1 C_{C\text{-}S}$, min^{-1}
k_2 = desorption-specific ratio rate constant, g · min^{-1}/surface $AlCl_3$
K_C = inverse adsorption constant for CCl_4, kP_C
M = molecular weight of CCl_4
P = pressure, kPa
r = reaction rate, g alumina reacted per g of alumina present per min, min^{-1}
R = gas constant
S = surface site
T = temperature, K
V = vacant site
Z = compressibility factor
α = model parameter, kPa^{-1}
ρ = density, g/cm^3

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