

A-6.4 Decomposition of CFCs by Supercritical Water

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Abstract Hydrolysis of CFCs in supercritical water(SCW) was studied to establish the process in which CFCs are completely hydrolyzed and hydrogen halides produced are neutralized. Decomposition of CFCs was increased with the density of SCW. Reaction rate increased with the pressure and strongly related with the static dielectric constant of SCW. Adding sodium hydroxide into SCW, reaction was promoted and hydrogen halides produced were neutralized to prevent the corrosion in the reactor.

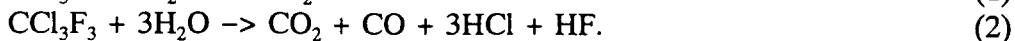
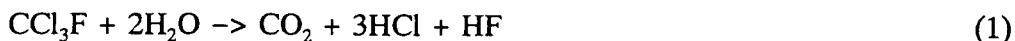
Key Words Supercritical Water, Hydrolysis, Chlorofluorocarbon, Freon, Decomposition

1. Introduction

Chlorofluorocarbons (CFCs) had been believed stable and nontoxic and they are used all over the world. However it has been cleared scientifically that CFCs emitted into atmosphere cause the depletion of stratospheric ozone layer and they are regulated internationally since 1989. Therefore, it is an urgent necessity to develop the safe and reliable destruction technology of CFCs.

While CFCs are very stable, it has been known that they are hydrolyzed slightly in water and the decomposition is promoted by existing metal and elevating temperature. In pyrolysis under a high temperature, many kinds of products including hazardous organic halide can be formed. Thus it is necessary to use a suitable catalysis for selective reaction or they must be decomposed at an extremely high temperature.

Supercritical water (SCW), at the temperature and pressure of which are higher than the criticals (374° C, 22.1MPa), provides an attractive reaction media the properties of which can be controlled to considerable degree by relatively small change in temperature or/and pressure. The properties of SCW above the critical temperature and pressure are different from normal liquid water and steam. Figure 1 shows static dielectric constant and ion product of water at 400° C as a function of pressure. Both the values are very small for high temperature and low pressure steam, i.e., ionic properties are lost. Pressurizing this steam above the critical pressure, they increase rapidly and static dielectric constant becomes comparable to a polar organic solvent and ion product larger than that of liquid water. Under such conditions, not only organic solvent including CFCs is miscible with SCW but also inorganic material can dissolve into it and dissociate into ions. In SCW, thus, hydrolysis that is ionic reaction can be promoted and CFCs can be decomposed completely as shown by equations



In this work, we have accomplished the hydrolysis of CFCs in SCW to develop the process in which CFCs are completely hydrolyzed and hydrogen halide produced are neutralized and any hazardous waste is not emitted.

2. Experimental

2.1 Batch-Type Microreactor

The hydrolysis of CFCs was tested using a stainless steel (SUS316) batch microreactor (16cm³), which was not equipped with the collector for gaseous products. The reactor was purged with argon and a desired weight of CFC and degassed and deionized water were loaded into it. After the reactor was placed in an electric furnace for required reaction time, it was quenched in an ice-water bath, opened, gas phase was collected with a syringe for analysis by a gas chromatograph and liquid content was recovered with rinsing the reactor by deionized water. Recovered solutions were analyzed with an ion chromatograph to determine the yields of fluoride and chloride ions.

2.2 Flow-type Reactor

Based on the results from batch experiments, a flow reactor shown in Fig.2 was assembled. The reactor was made of 1m length of 6.35mm O.D. x 1.24mm thickness Hastelloy C-276 tubing, 90cm length along which was heated by an electric heater. Only the inlet tube for CFC was made of platinum capillary tube and the other parts were SUS316. Deionized water was pressurized and preheated to desired reaction conditions. CFC was pressurized without preheating. The feed streams were mixed at the reactor inlet. The reactor effluent was cooled in an annulus heat exchanger. After depressurizing to atmospheric pressure through a back pressure regulating valve, the product stream was separated into aqueous and gas phases. Aqueous product samples were collected in receivers and analyzed using an ion chromatograph to determine the yield of halide ions. Gas product samples were analyzed using a gas chromatograph.

3. Results and Discussion

Hydrolysis of CFC-11, CFC-113 and carbon tetrachloride was tested using the microreactor. Figures 3-5 show the effect of water density loaded into the reactor on the yield of halide ions. The reaction times were 45 min except 30 min for carbon tetrachloride. In all experiments, the yields increased with the density. Carbon tetrachloride (Fig.3) was most reactive among the reagents tested and hydrolyzed completely at the density higher than 0.2 g/cm³. Defluorination for CFCs was harder than dechlorination but CFC-11 (Fig.4) and CFC-113 (Fig.5) were almost decomposed at the density higher than 0.4 g/cm³ and 0.5 g/cm³ respectively. Also, CFC-12 and CFC-13 were tested. CFC-12 was decomposed under almost same conditions as CFC-11 but CFC-13 was less decomposed than others.

Hydrolysis of CFC-11 was carried out using the flow reactor. Figure 6 shows the conversion of CFC-11 as a function of residence time. The reaction rate of CFC-11 increased with pressure as is evident from the Fig.6. Rate constants were determined from the slopes of the lines with the assumption of first order reaction. For example, at 380° C and 30MPa, it was 0.02 s⁻¹ and CFC-11 can be decomposed by more than 99% for few minutes of residence time. Rapid increase of the rate constant between 20MPa and 25MPa corresponds to the rise of the dielectric constant. The rate constant increased proportionally to static dielectric constant as shown in Fig.7, and the reason can be expressed that the hydrolysis of CFC, ionic reaction, is promoted with rising the polarity of SCW.

CO and small amount of chlorofluoromethanes and chlorofluoroethene were detected in gas products except CO₂ and CFC-11. Therefore, it is considered that CFC-11 was hydrolyzed mainly followed by Eq.(1), reduction of CO₂ with halogen acid produced CO and

small amount of halogenated carbon would produce with the effect of halogen acids because such byproducts hardly produced in the experiment with alkali described later.

Production of hydrogen halides with reaction is a serious problem for the corrosion in the reactor and under such condition, undesirable byproducts produced as before. Toxic hydrogen halides must be neutralized to avoid discharging into environment. Thus, sodium hydroxide was added into SCW to prevent the corrosion also to promote the hydrolysis. As shown in Fig.8 conversion increased with the concentration of sodium hydroxide and it increased by tow times at the equivalent concentration (0.12N) for CFC. The recovered solution was neutral and the concentration of metals dissolved in it decreased extremely. Therefore, the hydrolysis of CFCs using SCW with alkali can be an effective destruction method.

4. Conclusion

Hydrolysis of four CFCs and carbon tetrachloride using SCW was tested. While carbon tetrachloride was decomposed easily, CFC-13 was less decomposed, i.e., the more fluorinated CFCs, the harder to decompose. The reaction was accelerated with the density of SCW. CFC-11 can be decomposed by more than 99% for the residence time of few minutes at 380° C and 30MPa. Moreover, adding alkali into SCW, hydrolysis was promoted and the corrosion in the reactor was prevented. Thus, SCW hydrolysis of CFCs can be an effective destruction method.

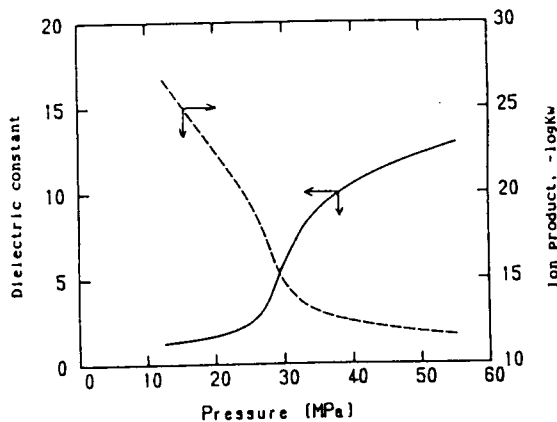


Fig.1 Dependence of dielectric constant and ionproduct on pressure

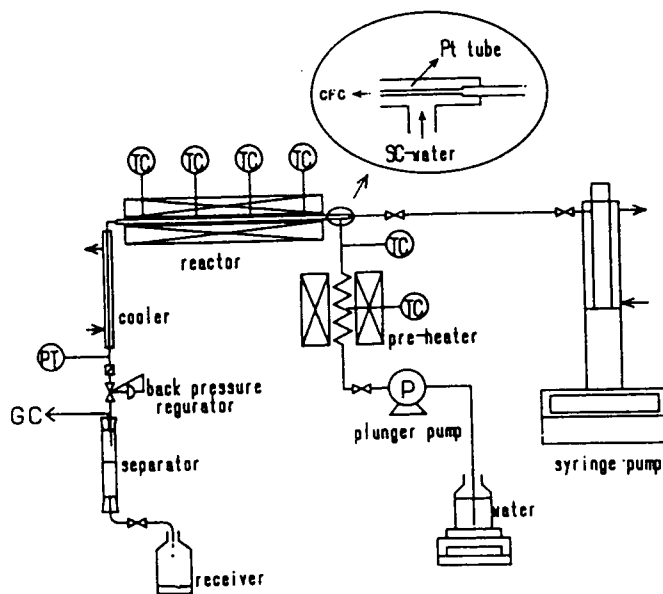


Fig.2 Schematic diagram of flow reactor

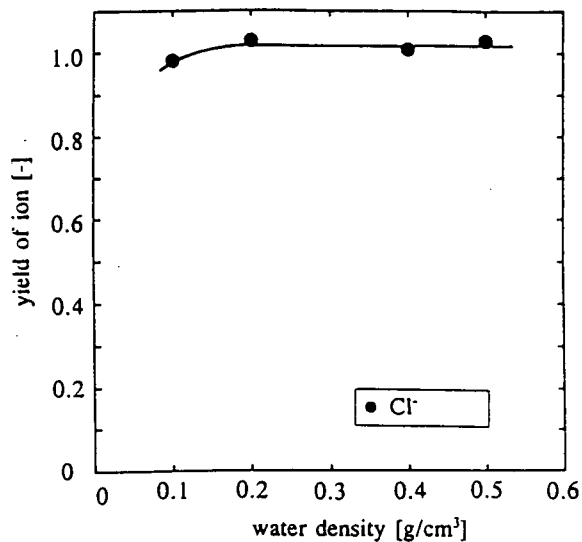


Fig.3 Hydrolysis of carbon tetrachloride

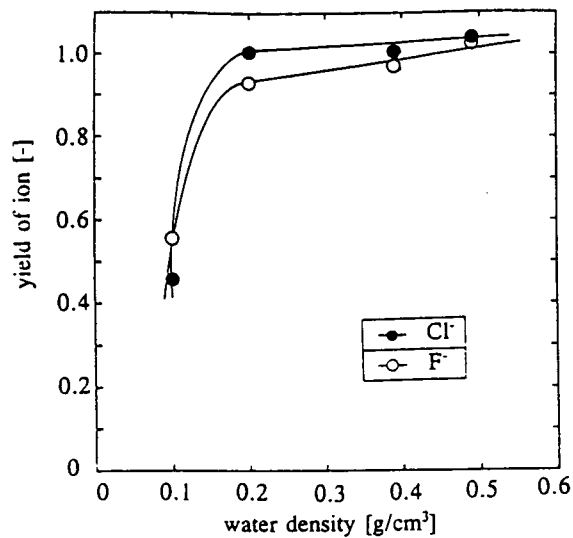


Fig.4 Hydrolysis of CFC-11

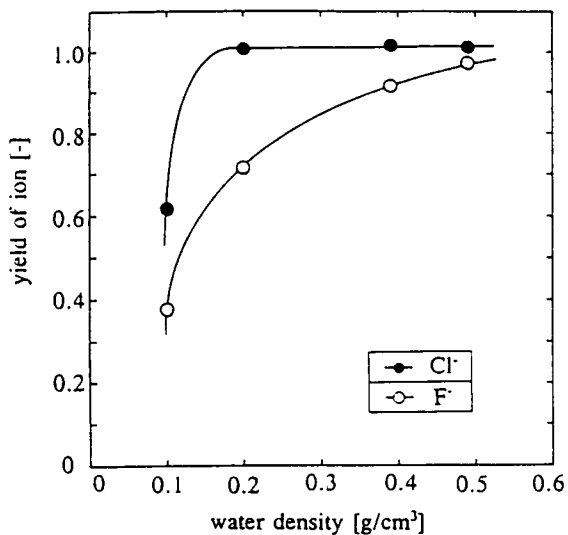


Fig.5 Hydrolysis of CFC-113

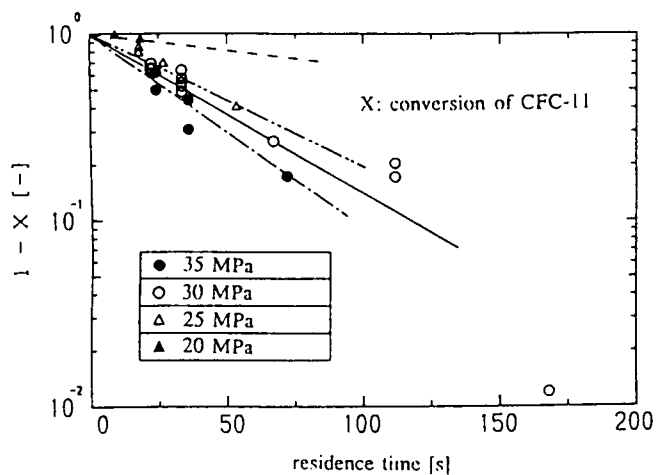


Fig.6 Effect of pressure on hydrolysis of CFC-11 at 380°C

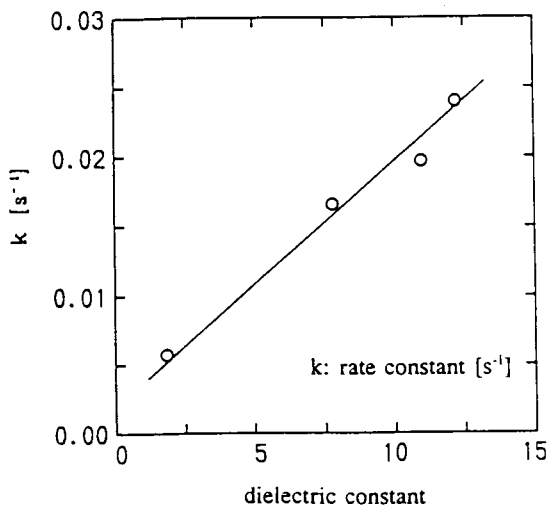


Fig.7 Relation between rate constant and dielectric constant

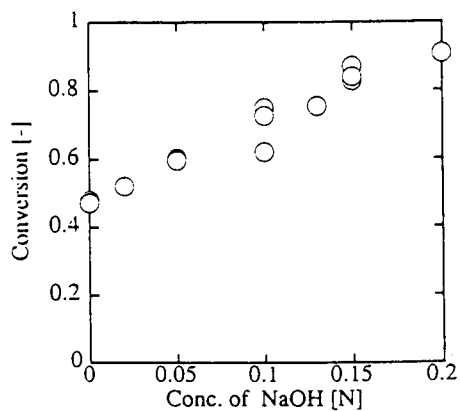


Fig.8 Effect of sodium hydroxide on Hydrolysis of CFC-11