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Catalytic pyrolysis of chlorodifluoromethane over metal fluoride catalysts to produce tetrafluoroethylene

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Abstract

The catalytic pyrolysis of chlorodifluoromethane ($CHClF_2$, R22) over aluminum fluoride, calcium fluoride and their physical mixtures were investigated. The conversion of R22 and the selectivity of tetrafluoroethylene (TFE) over prepared catalysts were compared with those over a non-catalytic pyrolysis. The conversion of R22 in the catalytic pyrolysis was significantly higher than that in the non-catalytic case under the tested conditions. In the catalytic pyrolysis of R22, the selectivity for trifluoromethane (CHF_3, R23) decreased with time-on-stream (TOS), whereas the selectivity for tetrafluoroethylene (C_2F_4, TFE) increased. The Cu-promoted catalysts were more selective toward TFE than Cu-unpromoted catalysts. It was found that the enhanced TFE yield over Cu-promoted metal fluoride catalysts may be explained by the increased heat transfer effect. The physical mixture catalysts showed the highest selectivity and yield for TFE. This result may be interpreted as due to the surface modifications, such as the formation of bimetallic fluoride and the variation of fluorine content on the surface of catalyst, caused by the attack of HF produced during the pyrolysis of R22.

Keywords: Chlorodifluoromethane; Tetrafluoroethylene; Pyrolysis; Metal fluoride; Aluminum fluoride; Calcium fluoride; Catalyst

1. Introduction

Chlorodifluoromethane ($CHClF_2$, R22) has been used as a refrigerant for air conditioners and as a raw material for the manufacturing of fluorinated compounds, such as tetrafluoroethylene (C_2F_4, TFE) and hexafluoropyropylene (C_3F_6, HFP). However, R22 is a controlled substance under the Montreal Protocol because of stratospheric ozone depletion potential and it has to be phased out by 2010 in developed countries. TFE has been used as a monomer for manufacturing fluorinated compounds, such as polytetrafluoroethylene (PTFE), commercially known as Teflon, and generally produced by the pyrolysis of chlorofluoroparaffins, especially R22, in the temperature range of 750–950 °C. A number of processes for the manufacturing of TFE have been reported [1–5]. The most widely used process for the commercial production of TFE is the direct pyrolysis of R22 [2,3]. The suggested mechanism of this process has been demonstrated to involve unimolecular extrusion of molecular HCl to form difluorocarbene ($:CF_2$), which dimerizes to form TFE [3–5].

R22 pyrolysis is a typical example of ultrapyrolysis or fast pyrolysis, where supplying heat is a critical factor. A tubular reactor has been used for the pyrolysis of R22. The conventional tubular pyrolysis shows low TFE yield due to the deficient supply of heat. Therefore, various heating media, such as superheated steam have been used [6]. Edwards and Small [7] reported a strong dependence upon the surface–volume ratio of the reactor of the conversion and the yield. The highly endothermic thermal pyrolysis of R22 consumes a large amount of energy. Because the pyrolysis of R22 is carried out at high temperature (>700 °C), there are some problems, such as the formation of coke and the corrosion of material caused by HCl and HF produced as by-products. Also, the conversion of R22 increases with increasing reaction temperature and/or residence time, but

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the yield of TFE decreases because of the increase of by-products [6,8]. To improve the relatively poor yield of TFE, especially at high reaction temperature, researchers introduced catalysts in the 1960s [9,10]. However, the enhanced yield of TFE has not been reported in the catalytic pyrolysis of R22. In previous works, results on the pyrolysis of R22 over activated carbon-supported Cu-based catalysts were reported [11–13]. The catalytic activities over the prepared catalysts were compared with those of a non-catalytic pyrolysis of R22. In addition, results on the manufacturing process of valuable fluorinated compounds, such as TFE, HFP and octafluorocyclobutane (cyclo-C_4F_8, RC318), were reported [14–16].

In this work, metal fluoride catalysts for catalytic pyrolysis of R22 were prepared by the fluorination of metal oxide with hydrogen fluoride. The catalytic pyrolysis of R22 over metal fluoride-based catalysts was carried out in a fixed-bed reactor system, and the effect of Cu adding on the catalytic properties was investigated.

2. Experimental

2.1. Preparation of metal fluoride catalysts

Metal fluoride catalysts were prepared by the fluorination of metal oxides with hydrogen fluoride (HF) [17]. Commercial hydrogen fluoride was supplied from Ulsan Chem. Co. The general procedure for the fluorination of aluminum oxides (Engelhard Co.) or calcium oxide (Junsei Chem.) is as follows. The reactor (0.0125 m o.d. and 0.25 m length) was charged with 20 g of alumina and placed in an electronic furnace. The furnace was gradually heated to 400 °C at a heating rate of 10 °C/min while nitrogen gas at a flow rate of 50 cc/min was passed through the reactor to remove all traces of water. The temperature was then lowered to 200 °C, and HF and nitrogen gases (1:4 molar ratio) were delivered to the reactor. From this point, the temperature was gradually raised to 450 °C and then maintained for 15–300 min. The effluent gas from the reactor was scrubbed with an aqueous sodium hydroxide solution to remove HCl and HF. The calcium fluoride was also prepared by the same procedure. In addition, the physical mixture catalysts (denoted as "Mixed" hereafter for abbreviation) of AlF_3 and CaF_2 (1:1 atomic ratio) were prepared. The physical properties of prepared catalysts are summarized in Table 1.

Table 1
Physical properties of metal fluoride catalysts prepared by the fluorination of metal oxide with HF

Catalyst	BET area (m^2/g)	Pore volume (cc/g)	Pore size (Å)
AlF_3[a]	35.13	0.181	177.66
CaF_2[b]	5.16	0.148	1142.25
Mixed[c]	23.53	0.157	284.07

[a] Prepared by the fluorination of γ-Al_2O_3.
[b] Prepared by the fluorination of CaO.
[c] Physical mixture of AlF_3 and CaF_2 (1:1 atomic ratio).

2.2. Preparation of Cu-promoted metal fluoride catalysts

Cu-promoted metal fluoride catalysts were prepared by impregnating copper on metal fluoride prepared by the fluorination of metal oxides. Cu–AlF_3, Cu–CaF_2 and Cu-mixed catalysts were prepared by a conventional impregnation method at room temperature. Dihydrated copper chloride (Kanto Chemical Co.) was used as the catalyst precursor. Copper chloride was dissolved with distilled water, and then this solution was poured into a vessel that contained a given amount of metal fluoride catalyst. The amount of copper was adjusted to be 10 wt.% of the amount of metal fluoride. After mixing at room temperature for about 24 h, the solution was slowly evaporated at 35–40 °C. Then the residue was dried in an oven at 110 °C for 12 h. The dried samples were calcined at 300 °C for 3 h and the calcined catalyst was reduced at 400 °C for 3 h in hydrogen flow before reaction.

2.3. Catalytic pyrolysis system

The pyrolysis of a diluted R22 (10% R22 in N_2-balance) over metal fluoride catalyst was carried out in the fixed-bed reaction system under the reaction temperature of 650 °C, space velocity of 15,000 h^{-1}, and atmospheric pressure. Before each pyrolysis experiment, each catalyst was pretreated with N_2 at 650 °C for 2 h. Fig. 1 shows the schematic diagram of the experimental system for the pyrolysis of R22. The gases were delivered with mass-flow controllers (Bronkhost, HI-TEC). The exit gases were analyzed with an on-line GC (DONAM Co., 6200) equipped with a TCD detector, using a Porapak Q column (0.003 m o.d. and 3 m length).

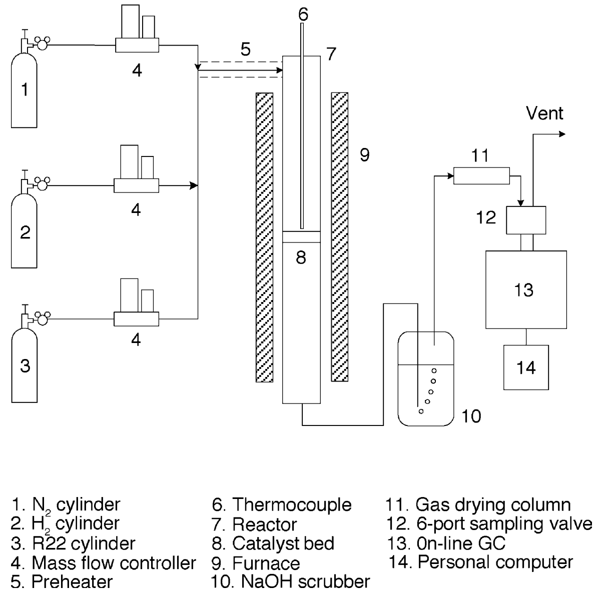

Fig. 1. Schematic diagram of the experimental system for the pyrolysis of R22.