

**Cu****TFE**

### A study on the pyrolysis of difluorochloromethane over Cu-based catalysts for synthesis of TFE(Tetrafluoroethylene)

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#### Introduction

Tetrafluoroethylene (C<sub>2</sub>F<sub>4</sub>, TFE) is a basic material used in the synthesis of fluorinated compounds, and also the monomer of an important polymer, commercially known as polytetrafluoroethylene (PTFE), Teflon. PTFE can be used in wide-ranging chemical, mechanical and electrical industries because of its excellent corrosion and heat resistant properties. Also it is highly resistant to wear and tear and has good antistick properties. A number of processes for the manufacture of TFE have been reported in literature [1-4]. The most widely used process for the commercial production of TFE is the direct pyrolysis of difluorochloromethane (CHClF<sub>2</sub>, R22).

The highly endothermic thermal pyrolysis of R22 consumes a large amount of energy. In addition, since the pyrolysis of R22 is carried out at high temperature (>700 °C), there exist some problems such as formation of coke, corrosive HCl and HF as a by-products. In order to improve relatively poor yield of TFE at low temperature, catalysts were introduced and their effects were studied [5,6]. However, significant increase of the TFE yield for pyrolysis of R22 using catalysts has not yet been reported. In this work, the pyrolysis of R22 over supported Cu-based catalysts were investigated to compare the Cu catalyzed pyrolysis with non-catalytic pyrolysis of R22.

#### Experimental

##### 1. Preparation of catalysts

Cu-based catalysts were prepared by impregnating copper on different supports such as  $\alpha$ -alumina,  $\gamma$ -alumina and activated carbon (denoted as "A.C" here after for abbreviation) which were inert under the corrosive reaction conditions because HCl and HF were formed during the pyrolysis. In this study, we mainly used CuCl<sub>2</sub>/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, CuCl<sub>2</sub>/A.C and Cu/A.C catalysts prepared by a conventional

impregnation method at room temperature. Copper chloride, dihydrate (Kanto Chemical Co.) was used as the catalyst precursor. Copper chloride was dissolved with distilled water and then this copper chloride solution was poured into a vessel where a given amount of support powder was filled. The amount of copper was adjusted to be 5 wt percent or 10 wt percent of support. After mixing at room temperature for about 24 hours, the solution was slowly vacuum evaporated at 35 - 40 . Then it was dried in an oven at 110 for 12 h. After drying, supported  $\text{CuCl}_2$  catalyst was prepared, and dried sample was calcined at 550 for 3h. Prior to use, the catalyst was reduced in hydrogen at 400 .

## 2. Reaction system

The pyrolysis of R22 over Cu-based catalysts was investigated in a fixed-bed reaction system under the reaction conditions, temperature 500-800 , residence time 0.05 sec and 10% R22 concentration in  $\text{N}_2$ -balance. The flow rates of R22 and  $\text{N}_2$  were controlled by mass flow controllers (Bronkhost, HI-TEC). The product mixture was analyzed by On-line GC (DONAM GC 6200) equipped with TCD detector and Porapak Q column (1/8in $\times$ 3m, sus)

## 3. Catalyst characterization

The structural analyses of catalyst surfaces were conducted by XRD (X-ray diffractometer, MXP3A-HF, MAC Science Inc.) using  $\text{Cu K}\alpha$  radiation (40kV, 30mA) and EDS (energy dispersive X-ray spectrometer, RONTEC Inc. EDWIN M1). The crystalline phases were identified by the comparison of measured XRD patterns of the catalysts with JCPDS powder diffraction file data.

## **Results and Discussion**

### 1. Non-catalytic pyrolysis of R22

Non-catalytic pyrolysis of R22 was carried out using a dilute R22 (10% R22, in  $\text{N}_2$ -balance) in the temperature range from 550 to 800 . R22 conversion of 91% corresponding to TFE yield of 76% was obtained at 750 . Maximum TFE selectivity of 98% was obtained at 650 and 700 . Above 700 the selectivity for TFE decreased with increase of temperature. 20% and no dilute R22 were introduced to study the effect of  $\text{N}_2$  dilution on the conversion of R22 and selectivity for TFE. With increasing the dilution ratio, the conversion of R22 and selectivity for TFE increased. Also at higher reaction temperature the difference became larger.

### 2. Catalytic pyrolysis of R22 over $\text{Cu}/\text{Al}_2\text{O}_3$ .

In order to study effects of support material, catalytic reactivity of Cu on various supports was compared. We chose supports like  $\alpha\text{-Al}_2\text{O}_3$  and  $\gamma\text{-Al}_2\text{O}_3$ , because they have excellent corrosion and heat resistant properties in high reaction temperature. 5wt%  $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$  was tested at 500 and showed R22 conversion of 80%. However, no TFE was found. This is believed due to the decomposition of R22. Effects of temperature on conversion, selectivity and yield for TFE over Cu-based

catalysts supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are shown in Fig. 1 (A). Results of non-catalytic pyrolysis under the same conditions are also shown in Fig. 1 for comparison. R22 conversion increased with increase of temperature and this was similar to non-catalytic pyrolysis. Maximum selectivity to TFE was obtained at 600 and 650 . Among  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> based catalysts, Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was the most active catalyst. But Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> showed lower reactivity compared to non-catalytic pyrolysis.

XRD and EDS were employed to characterize compounds formed in catalyst during pyrolysis of R22. It was found that Cl peaks were detected in used Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst from EDS analysis. Fig. 2 (A) shows XRD of fresh CuO/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and used Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> after reaction. In fresh catalysts, peaks corresponding to cupric oxide and  $\alpha$ -alumina were observed. But as shown in Fig. 2(A), no peak corresponding to CuO was detected in used catalyst and new peaks were observed. After comparison with data on XRD peaks of various materials those new peaks could be attributed to aluminum fluoride, AlF<sub>3</sub>. This can be explained by reaction between  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and HF.

### 3. Catalytic pyrolysis of R22 over Cu/A.C.

Fig. 1(B) shows the conversion, selectivity and yield for TFE over A.C based catalysts as a function of the reaction temperature. Reactivity of Cu/A.C was much higher than CuCl<sub>2</sub>/A.C catalyst for all reaction temperatures as indicated by TFE yield in Fig. 1(B). In addition, the effects of Cu contents in Cu/A.C are also shown in Fig. 1(B). R22 conversion and yield for TFE increased with increasing Cu contents. 10 wt% Cu/A.C catalyst showed similar yield for TFE compared to non-catalytic pyrolysis. At 700 , TFE yield in the catalytic pyrolysis of R22 over 10wt% Cu/A.C catalyst was much higher than that in the non-catalytic. EDS analysis indicated that fresh 10wt% Cu/A.C catalyst contained Al, Si, Cl, Ca and Fe as impurity. These elements were also observed at activated carbon. The XRD patterns of fresh and used 10wt% Cu/A.C catalysts are shown in Fig. 2 (B). On the used catalyst, peaks corresponding to either CaAlF<sub>5</sub> or Ca<sub>2</sub>AlF<sub>7</sub>, or their mixture were detected. It is thought that Ca, Al-containing activated carbon was gradually converted into CaAlF<sub>5</sub> or Ca<sub>2</sub>AlF<sub>7</sub> during the pyrolysis of R22. Although fluoride compounds were formed by reaction by-product, HF, there was no significant decrease of TFE yield in the catalytic pyrolysis of R22.

## References

1. J. D. Park, A. F. Benning, F. B. Downing, J. F. Laucius, and R. G. Mcharness, *Ind. Eng. Chem.*, **39**, 354(1947).
2. Venkateswarlu, Y. and P. S. Murti, *Chem. Proc. Eng. Oct.*, 25(1970).
3. M. Han, B. S. Kim, C. U. Kim, and J. M. Lee, *J. Korean Ind. Eng. Chem.*, **10**, 190(1999).
4. P. B. Chinoy and P. D. Sunavala, *Ind. Eng. Chem. Res.*, **26**, 1340(1987).
5. K. S. Revell, Brit. Patent, 983,222
6. Daikin Kogyo, Brit. Patent 1061,377

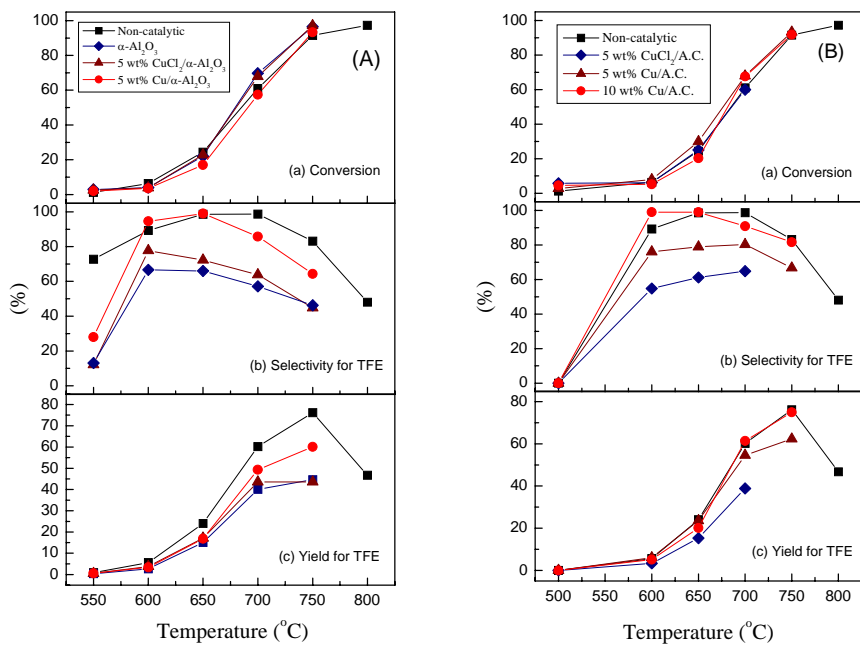


Figure 1. Effects of temperature on conversion, selectivity and yield for TFE over Cu-based catalysts.

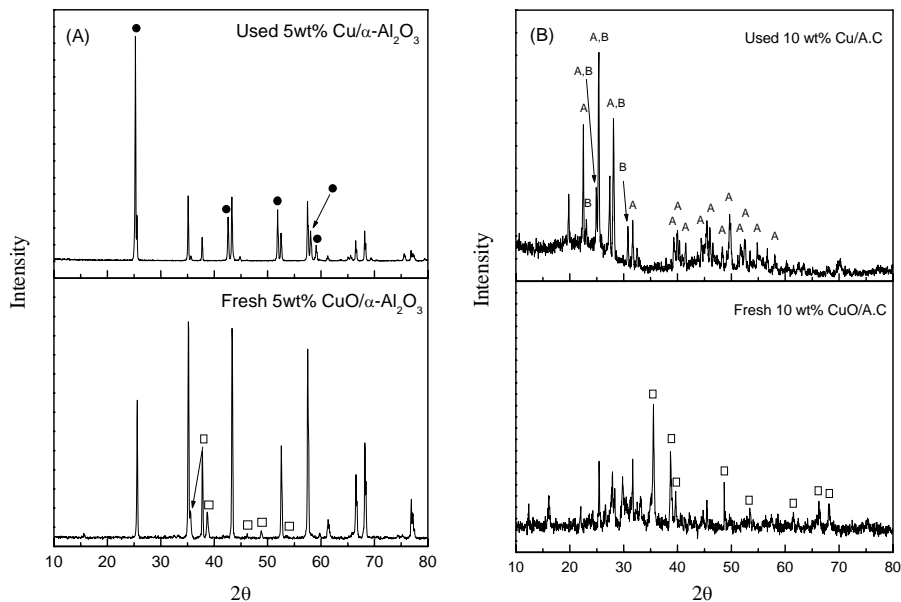


Figure 2. XRD patterns of fresh and used catalysts. (  $\bullet$  : Aluminum fluoride,  $\square$  : Cupuric chloride dihydrate, A: CaAlF<sub>3</sub>, B:Ca<sub>2</sub>AlF<sub>7</sub>)