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Catalytic Decomposition of Dichlorodifluoromethane (CFC-12) Over MgO/ZrO$_2$ Solid Base Catalyst
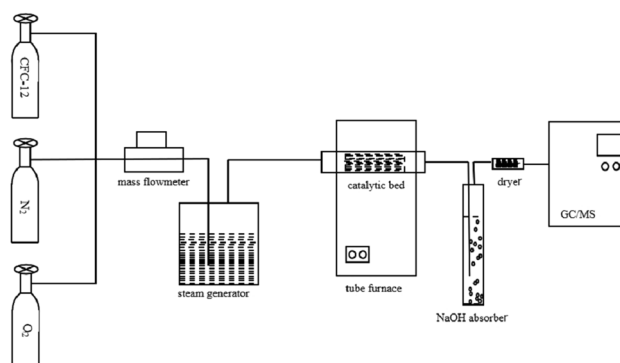
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Abstract

MgO/ZrO$_2$ solid base catalyst was prepared by co-precipitation method. The effects of hydrolysis temperature, water vapor concentration, total flow rate and calcination temperature of the catalyst on the decomposition rate of dichlorodifluoromethane (CFC-12) were studied. The results showed that the decomposition rate of CFC-12 could reach 98.90% by using MgO/ZrO$_2$ solid base as the catalyst at a hydrolysis temperature of 400 °C, a water vapor concentration of 25%, a total flow rate of 5 mL/min and a calcination temperature of 700 °C. The XRD characterization of the catalyst under different calcination temperature showed that the MgO/ZrO$_2$ catalyst was a solid solution. The products were tested by ion chromatography, SEM and EDS and finding that the decomposition products were main HCl, HF and CO$_2$.

Graphical Abstract

Keywords MgO/ZrO$_2$ · Solid base catalyst · CFC-12 · Decomposition rate

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1 Introduction

Chlorofluorocarbons (CFCs) had been widely used as refrigerants, solvents, propellants, blowing agents [1], ect. However, CFCs are not only the main culprits for the destruction of the ozone layer but also greenhouse gases which can warm up our earth [2–8]. It is necessary to prohibit CFCs into atmosphere and convert CFCs into useful and less environmentally harmful substances [9]. So, the CFCs decomposition has attracted considerable public enthusiasm. A lot of decomposition approaches (such as incineration, cement kiln, high frequency-induced plasma, super critical water, and etc.) have been developed [1]. Among these methods, the catalytic hydrolysis

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method has some unique advantages: (1) the decomposition temperature is lower than other methods; (2) the reactant H_2O is easily obtained; (3) the process is simple; (4) The main degradation products are HF, HCl and CO_2 which can be easily removed by neutralization of lye or alkaline solid waste. Obviously, the appropriate catalyst is an important factor to the decomposition rate of CFCs.

The preparation of Freon decomposition catalysts, structural properties, decomposition process conditions, stability of decomposition products have been carried out and many advances have been developed [10, 11]. K. Yanagisawa et al. first investigated the catalytic hydrolysis of Freon by Y-type molecular sieves [12, 13]. The results showed that the initial activity of the Y-type molecular sieve catalyst is very high. But it was easily inactivated. Then, the catalytic performance of the metal oxide/fluoride catalyst was examined and it was found that the activity of the titanium oxide catalyst was better. Zheng et al. investigated the catalytic activity of gold catalyst at 400–700 °C [14]. It was found that Au/Al_2O_3 catalyst can hydrolyze CFC-12 at 500 °C, but there is still no stability data related to Au/Al_2O_3 catalyst. Mill et al. examined acidic catalysts (such as SiO_2/Al_2O_3, TiO_2/SiO_2, BPO_4) and considered that BPO_4 was better [15]. The composite catalyst PO_4–ZrO_2 can hydrolyze CFC-12 at lower temperature. There are also reports on describing the use of noble metal or oxide catalysts for the catalytic hydrolysis of Freon, which consists of a wide range of metals and metal oxides [16]. Catalytic decomposition is very promising because of simple processes, requiring mild conditions. CFC-12 is one of the most widely used gases in all CFCs. Solid base catalysts were found to be effective for the decomposition of CFC-12. It is well-known that solid base catalysts have many advantages. They are noncorrosive and present fewer disposal problems, while allowing easier separation and recovery of the products, catalysts, and solvent. Thus, solid base catalysts offer environmentally benign and more economical pathways for the synthesis of fine chemicals [17]. So it has become a popular material for the catalytic decomposition of CFC-12.

In this study, MgO/ZrO_2 solid base was selected as the catalyst to study the effects of reaction conditions such as hydrolysis temperature, water vapor concentration, total flow rate and calcination temperature of the catalyst on the decomposition rate of CFC-12. XRD characterization was used for the catalyst of different calcination temperature and ion chromatography, SEM and EDS analysis were used for the product analysis.

2 Experimental

2.1 Catalyst Preparation

The MgO/ZrO_2 catalyst was prepared by co-precipitation method using $ZrOCl_2 \cdot 8H_2O$ and $MgCl_2$ as raw materials.

Aqueous ammonia was used as a precipitant, and the pH was adjusted to 8–9. The mixed precipitate was stirred well for 4 h and aged for 24 h. Then the precipitate was washed with distilled water to remove Cl^- and calcined in a muffle furnace at 700 °C for 4 h [18–21]. A solid base catalyst of MgO/ZrO_2 was obtained and applied to the catalytic decomposition of CFC-12.

2.2 Catalytic Decomposition of CFC-12

1.00 g MgO/ZrO_2 solid base catalyst and 170 g quartz sand was used as a catalyst carrier to fill the quartz tube. The simulated gas composition (mol%): 1.0 CFC-12, 25.0 H_2O (g), 5.0 O_2 and N_2. Effluent gases were passed through NaOH solution to eliminate HF and HCl produced during the reaction. After the reaction for 30 min, samples were taken and analyzed by gas chromatography/mass spectrometer (ThermoFisher GC/MS) to calculate the decomposition rate (Fig. 1).

2.3 Catalyst Characterization

X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer using Cu Kα radiation with 40 kV and 40 mA, scan speed 12°/min and scan range 10–75°.

2.4 Analytical Method

Gas chromatography-mass spectrometry (GC/MS) was used for quantitative and qualitative analysis. The instrument is Thermo Fisher (ISQ) manufactured by Thermo- Fisher Scientific, Inc. The column is capillary column (100% dimethyl polysiloxane) manufactured by Thermo Fisher Scientific; detection conditions: inlet temperature is 80 °C, column temperature is 35 °C, retention time is 3 min, carrier gas is high purity He (He ≥ 99.999%), flow rate of 1.00 mL/min in constant flow mode, split ratio is 140:1, The mass spectrometer detector is an EI source, with an electron energy of 70 eV, an ion source temperature of 260 °C, an ion transport rod temperature of 280 °C, and an injection volume of 0.1 mL. Qualitative and quantitative analysis of CFC-12 was performed under this analysis condition. The catalytic decomposition effect was mainly evaluated by the conversion rate of CFC-12 and the total yield of CO and CO_2, and the calculation was as follows: [Yield of COx] = [COx]out/([CFC-12]in-[CFC-12]out) × 100%; [Conversion of CFC-12] = ([CFC-12]in-[CFC-12]out)/[CFC-12]in × 100%.
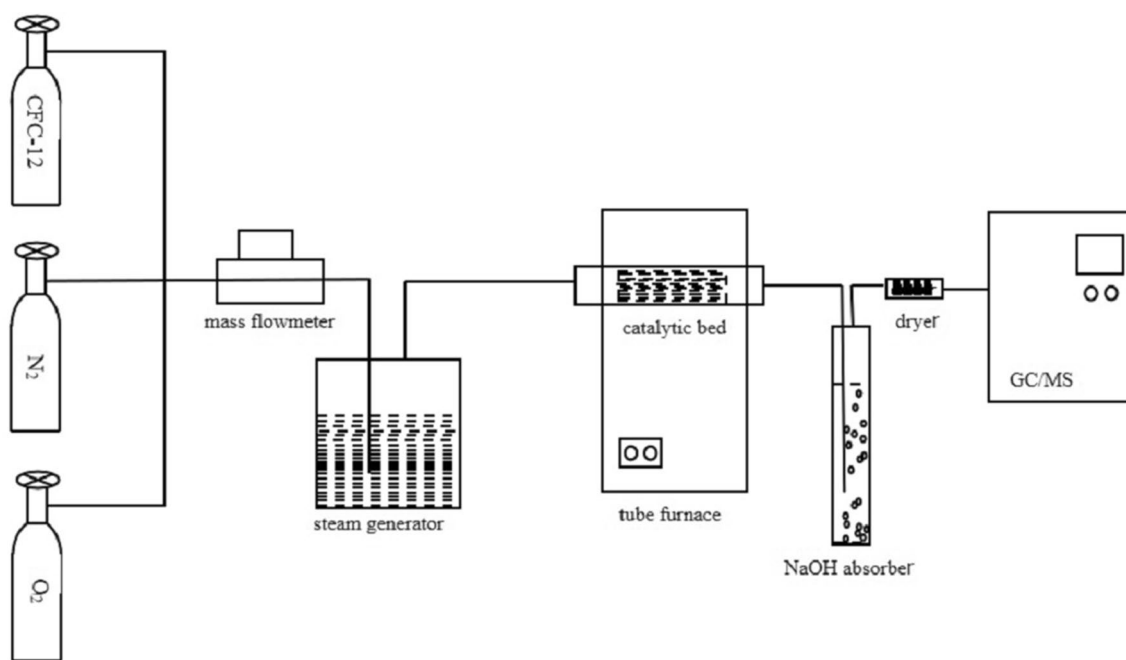
Fig. 1 Flow diagram of CFC-12 catalytic decomposition experiment

3 Results and Discussion

3.1 Effect of Hydrolysis Temperature on Decomposition Rate

The effect of catalytic hydrolysis temperature on the decomposition rate of CFC-12 was investigated. The water vapor concentration was 25% and the total flow rate was 5 mL/min. The results are shown in Fig. 2. With the increase of temperature, the decomposition rate of CFC-12 gradually increases and reaches a maximum of 93.27% at 400 °C. This is due to the decomposition reaction of CFC-12 at medium and low temperatures. The reaction is:

$$CCl_2F_2 + H_2O \rightarrow CO + 2HCl + 2HF \tag{1}$$
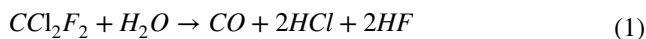
This reaction is an endothermic reaction. As the temperature increases, the chemical equilibrium shifts to the right, resulting in a gradual increase in the decomposition rate of CFC-12. It shows that CFC-12 conversion is more thorough. From the reaction Eq. (1), theoretically, 1 mol CO is produced for every 1 mol CFC-12 consumed, but the graph shows that the actual CO yield is far lower than the theoretical value, which is due to the reaction:

$$2CO + O_2 \rightarrow 2CO_2 \tag{2}$$

CO$_2$ is generated, resulting in a lower CO yield. The products are HCl, HF, CO and CO$_2$. O$_2$ in the reaction formula is mainly derived from dissolved oxygen in the water, and
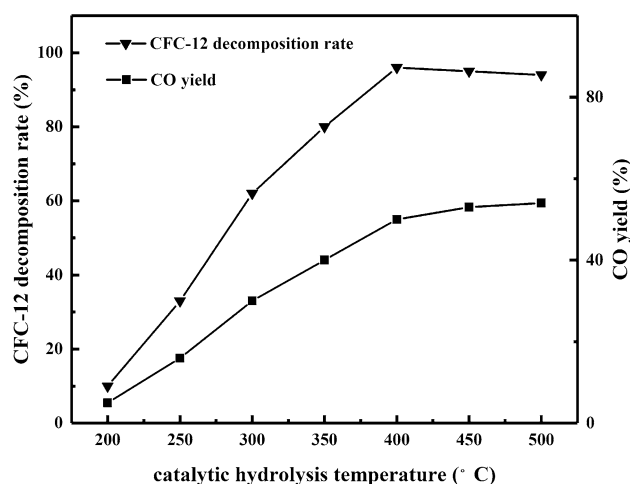

Fig. 2 Effect of hydrolysis temperature on decomposition rate

air in the reaction bed before the reaction. In summary, the optimal catalytic hydrolysis temperature is 400 °C.

3.2 Effect of Water Vapor Concentration on Decomposition Rate

The effect of water vapor concentration on the decomposition rate of CFC-12 was investigated. The reaction temperature was 400 °C and the total flow rate was 5 mL/min. The results are shown in Fig. 3. CFC-12 decomposition rate is only 26.18% without water vapor. As discussed above, the

Fig. 3 Effect of water vapor concentration on decomposition rate
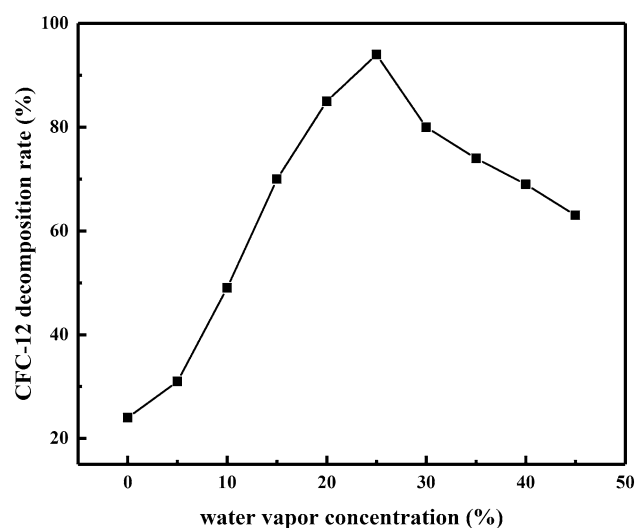
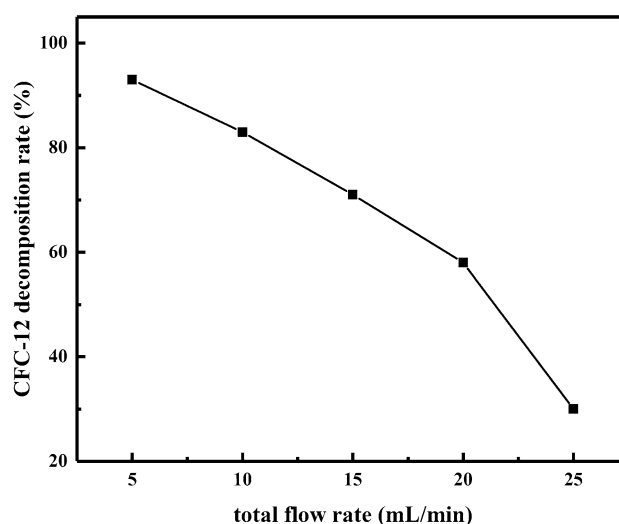**Fig. 4** Effect of total flow rate on decomposition rate

probability for reaction (1) is very little with a small amount of water vapor in the air. Since the electronegativity of the fluoride ion is greater than the chloride ion, the chloride ion in CFC-12 (CCl_2F_2) is likely to be replaced by the fluoride ion in HF and producing a by-product CFC-13 ($CClF_3$). The substitution reaction is:

$$CCl_2F_2 + HF \rightarrow CClF_3 + HCl \tag{3}$$

Decomposition reaction of CFC-12 is a hydrolysis reaction and there is no participation of water vapor, and CFC-12 cannot be decomposed completely. With the increase of water vapor, the probability for reaction (1) turns larger and the decomposition rate gradually increases. When the water vapor concentration is 25%, the decomposition rate reaches a maximum of 94.88%. This further demonstrates that the decomposition reaction of CFC-12 is a hydrolysis reaction. When the vapor concentration exceeds 25%, the decomposition rate begins to decline. This is due to that the increasing water vapor concentration would lead to an increase in the total flow rate of gas, insufficient contact of CFC-12 with the catalyst, blow-out of the reaction. Moreover, the influx of large amounts of water vapor also results in dehydration of the catalyst and loss of active ingredients.

3.3 Effect of Total Flow Rate on Decomposition Rate

The effect of the total flow rate on the decomposition rate of CFC-12 was investigated with the reaction temperature of 400 °C and the water vapor concentration of 25%. As shown in Fig. 4, the total flow rate has a great influence on the decomposition rate of CFC-12. With the increase of the flow rate, the decomposition rate decreases linearly. This is mainly due to the fact that the catalytic reaction of CFC-12

is gas–solid reaction. When the flow rate increases, the contact time between CFC-12 and the catalyst decreases. The reaction is incomplete, leading to a decrease in the degradation rate. The optimal total flow rate of MgO/ZrO_2 for the decomposition of CFC-12 is 5 mL/min.

3.4 Effect of Calcination Temperature on Decomposition Rate

The effect of calcination temperature on the decomposition rate of CFC-12 was investigated. The results are shown in Fig. 5. With the increase of calcination temperature, the decomposition rate of CFC-12 increased gradually. When the calcination temperature was 700 °C, the decomposition rate reached 98.90%. With further increasing the calcination temperature, the decomposition rate decreased significantly. Because the temperature is over 700 °C, the structure of the catalyst is changed, and the ZrO_2 is converted from a tetragonal phase to a monoclinic phase, which reduces the activity of the catalyst. Therefore, it is suitable to select a calcination temperature of 700 °C.

3.5 Catalyst Characterization

Figure 6 shows the XRD patterns of MgO/ZrO_2 solid base catalyst calcined at different temperatures. The crystal phase of ZrO_2 is mainly in the form of a tetragonal phase. When the calcination temperature reached 800 °C, monoclinic phase ZrO_2 appears, but the diffraction peak intensity of monoclinic phase ZrO_2 was weak, XRD characterization was the mixed state of tetragonal phase and monoclinic phase, and the diffraction peak of MgO was not detected. In this solid base system, Mg^{2+} enters the lattice of ZrO_2 to
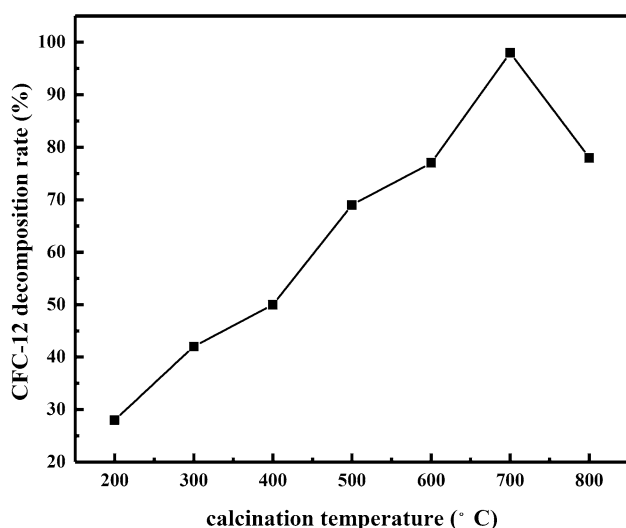
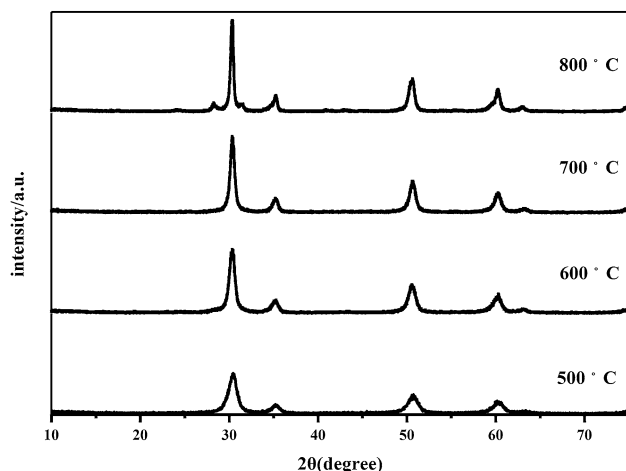**Fig. 5** Effect of calcination temperature on decomposition rate

Fig. 6 XRD pattern of MgO/ZrO$_2$ solid base catalyst calcined at different temperature

replace the position of Zr^{4+}, thereby stabilizing the crystal form of the tetragonal phase ZrO$_2$ to form a MgO/ZrO$_2$ solid solution structure. As the calcination temperature increases, the diffraction peak of ZrO$_2$ is only slightly enhanced, indicating better crystallinity at higher temperature.

3.6 Product Analysis

3.6.1 Ion Chromatography Analysis of the Product

The change in the temperature of catalytic hydrolysis between Cl$^-$ and F$^-$ in the product was examined and the results are shown in Fig. 7.

As shown in Fig. 7, the concentration of Cl$^-$ and F$^-$ increases with the increase of catalytic hydrolysis temperature. In theory, the concentration of F$^-$ is higher than the concentration of Cl$^-$. But the experimental result shows that the concentration of Cl$^-$ is higher than that of F$^-$, which is due to the fluorination produced in the catalytic process causes fluorine to enter the catalyst. This result also proves that the catalytic degradation products are HF and HCl.

3.6.2 SEM and EDS Analysis of the Degradation Product

Figure 8 is SEM image and EDS spectrum of product after reaction for 15 h at 400 °C. NaOH solution was used to absorb the exhaust gas. From the SEM image, it can be seen that the particles is amorphous and of thin slice. Five elements of carbon (C), oxygen (O), fluorine (F), sodium (Na), and chlorine (Cl) can be found in this EDS spectrum and no other heteroelements can be observed. The sample is composed of NaF, NaCl and Na$_2$CO$_3$, which are obtained by reaction between degradation products and NaOH. This further shows that the degradation products are main HCl, HF and CO$_2$.

4 Conclusions

MgO/ZrO$_2$ solid base was used as a catalyst to degrade CFC-12, the maximum decomposition rate could reach 98.90% under the condition of which catalytic hydrolysis temperature was 400 °C, the water vapor concentration was 25%, the total flow rate was 5 mL/min and the calcination temperature was 700 °C. The results of ion chromatography, SEM and
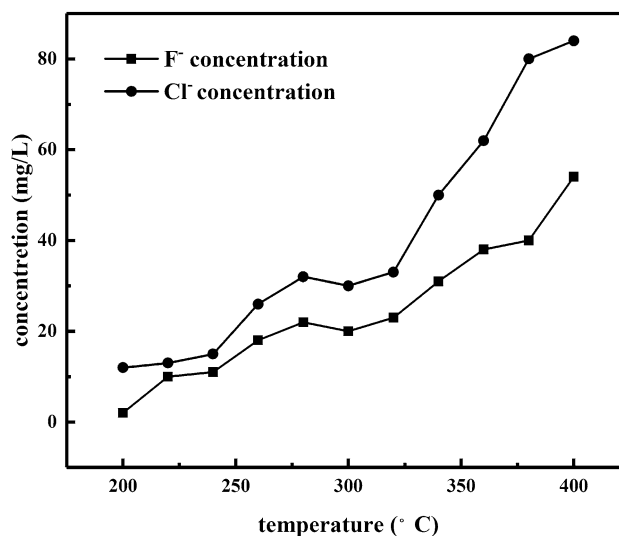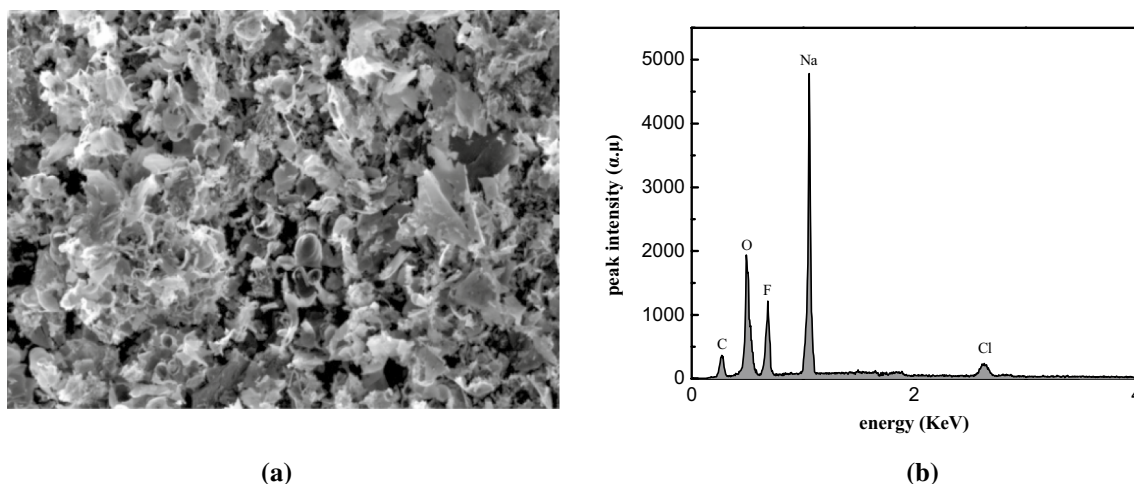

Fig. 7 Ion chromatography analysis of the product

(a)

(b)

Fig. 8 SEM image and EDS spectrum of the degradation product

EDS analysis indicate that the decomposition products are main HCl, HF and CO_2.

Compliance with Ethical Standards

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