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The reaction of $MgCl_2\cdot4H_2O$ with CCl_2F_2

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Abstract

A new reaction of $MgCl_2\cdot4H_2O$ with CCl_2F_2 is investigated by DTA and TG from room temperature to 350 °C. It is observed that MgF_2 was obtained between 252 and 350 °C, Below the temperature, $MgCl_2\cdot4H_2O$ dehydrates and hydrolyzes to $MgCl_2$ and Mg(OH)Cl, which are the real reactants of the reaction with CCl_2F_2. The formation of MgF_2 is ascribed to the reaction of $MgCl_2$ and Mg(OH)Cl with HF, which forms by decomposition of CCl_2F_2 with the taking part in of H_2O released from dehydration of hydrated magnesium chloride on the surface of $MgCl_2$ and Mg(OH)Cl, which catalyzes the decomposition of CCl_2F_2 in this case. Consequently, the reactions are tested in the fluid-bed condition. It is found that MgF_2 formed at temperatures down to 200 °C in a fluid-bed reactor. This reaction may be used as a method of disposing of the environmentally sensitive CCl_2F_2 (rather than release into the atmosphere). It is also a method for the preparation of MgF_2.

Keywords: MgF_2; $MgCl_2\cdot4H_2O$; CCl_2F_2; Catalytic decomposition; Thermal analysis; Fluid-bed

1. Introduction

In our laboratory, we found that $MgCl_2\cdot6H_2O$ could react with CCl_2F_2 by heating to form MgF_2. This is a new reaction that had not previously been reported. Moreover, this reaction has potential uses as a method to manufacture MgF_2 and as a method for depletion of CCl_2F_2, which damages the layer of ozone in the atmosphere. So it is appropriate to make further investigations of the novel reaction by all possible means. $MgCl_2\cdot6H_2O$ is not stable to heat. It can dehydrate stepwise through $MgCl_2\cdot xH_2O$ ($x = 4, 2, 1, 0$) and hydrolyze to Mg(OH)Cl, and eventually $MgCl_2$ and Mg(OH)Cl transform to MgO at high temperature when O_2 is present. The process of dehydration of $MgCl_2\cdot6H_2O$ by heating [1–4] was previously studied in static air and in flow N_2 and HCl. It is known that CCl_2F_2 is much more thermally and chemically stable even at higher temperature, it does not decompose even at 500 °C in the absence of catalysts. So the aim and purpose of the present work is to identify which substance has reacted with CCl_2F_2 and why and how it reacts with $MgCl_2\cdot6H_2O$. DTA and TG analysis, which are based on the changes of heat of the reactions of interest and the changes of mass of the system investigated, respectively, provide a conventional method to study a multi-step reaction. So in this work we report the results of the investigation a non-isothermal process of $MgCl_2\cdot4H_2O$ (which was from drying $MgCl_2\cdot6H_2O$) in CCl_2F_2 using DTA/TG method. With the previous investigations about the decomposition of CCl_2F_2 [5–7], the mechanism of the reaction is discussed according to the result of our thermal analysis.

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To investigate the possibility of the practical uses of the reaction, it was carried out in fluid-bed reactor. With large gas flow rate, a non-isothermal process with high ratio of CCl_2F_2/air and two isothermal processes with low ratio of CCl_2F_2/air were investigated and the results discussed.

2. Experimental

2.1. Materials

$MgCl_2 \cdot 6H_2O$ used this work was AR regent, from Xi'an chemical regent factory, Xi'an city, PR China. It was analyzed to contain 63% water and corresponds to $MgCl_2 \cdot 9.01H_2O$. For thermal analysis, the material was powdered and dried at 90 °C for 24 h, the product analyzed as $MgCl_2 \cdot 4.04H_2O$. The material used in the fluid-bed experiment was the AR $MgCl_2 \cdot 6H_2O$ without further treatment and the average particle magnitude was 1.5 mm. The CCl_2F_2 with high purity was bought from Shanghai No. 2 Light Industry Company, Shanghai, PR China. Highly pure N_2 used in DTA and TG was obtained from Qinghai Oxygen-Making Factory, Xining City, PR China, stored in high-pressure bomb. Air, comparatively dry due to the dry climate of our region, was not treated further before used.

2.2. Thermoanalytical experiments

The DTA and TG curves of the reactions $MgCl_2 \cdot 4H_2O$ with CCl_2F_2 were recorded on a Setaram TG/DTA-92 analyzer from room temperature to 350 °C. The fine sample was used and the amount of sample was 4.10 mg (less than ordinary amount 10 mg). The sample was loaded in Al_2O_3 crucible and just covered the bottom of the crucible to allow an ample contact between solid and gas. The heating rate of the oven was controlled at 2.5 °C min^{-1} to avoid the overlapping of peaks. CCl_2F_2 flew through the samples in the furnace and N_2 was used to prevent CCl_2F_2 from entering the balance.

2.3. The fluid-bed reacting experiments

This reaction was carried out in a glass fluid-bed. The gas was preheated in a tube furnace before been directed into the fluid-bed, which is open to the atmosphere. The non-isothermal experiment extended from room temperature to 300 °C. The CCl_2F_2 flow rate was 700 nl h^{-1}, and air flow rate was lowered from 1000 to 300 nl h^{-1} to maintain the sample in conventional fluid state, i.e. the ratio of CCl_2F_2 to air is from 0.7:1 to 2.3:1. The products from reactions at different temperatures are analyzed by titration with EDTA, $Hg(NO_3)_2$ and Karl Fischer regent for their Mg, Cl and water contents, respectively. The isothermal experiment was carried out in the same fluid-bed by the same procedure, the temperature being controlled at 200 or 250 °C, respectively, with the ratio of CCl_2F_2 to air at 1:10. The percentages of MgF_2 in products of reaction after different period of times were obtained by washing the residual phases with HCl solution, drying and weighing. The soluble material was identified by chemical analysis and the residue was identified to be MgF_2 by X-ray diffraction.

3. Results and discussion

3.1. Characteristics of the reaction of $MgCl_2 \cdot 4H_2O$ with CCl_2F_2

Hydrated magnesium chloride used in DTA/TG analysis was previously dried to $MgCl_2 \cdot 4.04H_2O$. The TDA and TG responses for the dried material in CCl_2F_2 are exhibited in Fig. 1. The corresponding mass losses for the peaks in TG curve were shown in Table 1.

In the DTA curve, the three endothermal peaks α, β, γ, are the dehydration of $MgCl_2 \cdot 4H_2O$. In comparison with the report of Xia and Wang [1], in which

Table 1
Peaks in DTA and corresponding weight loss in TG

Peak name	Endo/exo	Temperature (°C)	Measured mass loss (%)
α	Endo	139	22.44
β	Endo	172	12.68
γ	Endo	233	13.17
δ	Exo	291	16.34
ε	Exo	316	16.34

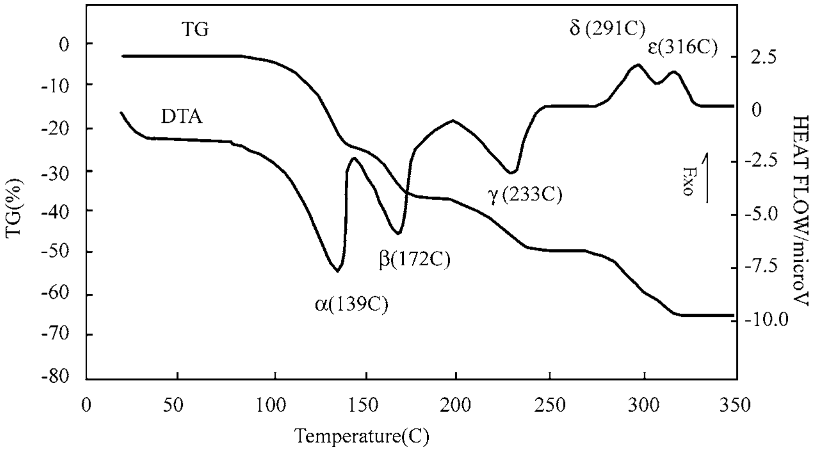
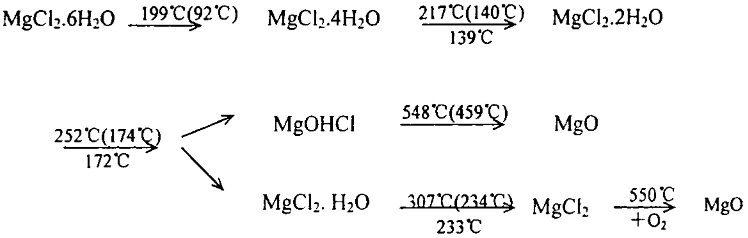


Fig. 1. DTA and TG curve of $MgCl_2·4H_2O$ in CCl_2F_2.

it is suggested that $MgCl_2·6H_2O$ dehydration can proceed:



where the temperatures above the arrows report the results in static air and the results in flowing N_2 (are in the parentheses) and the temperatures of this work are shown under the arrows. The corresponding expected weight losses for the peaks α, β and γ on the basis of the steps of dehydration of $MgCl_2·4H_2O$ to $MgCl_2$ agree with the values determined. So we can confirm that $MgCl_2·4H_2O$ does not react with CCl_2F_2 until 250 °C, and as in the flow N_2 only dehydrates and hydrolyzes to $MgCl_2$ and Mg(OH)Cl.

The two exothermic peaks between 252 and 350 °C corresponds the reaction of forming MgF_2, there are two the reactions taking place in the system, the two reactants being identified as $MgCl_2$ and Mg(OH)Cl. Assuming a total conversion of $MgCl_2·4H_2O$ to MgF_2, the calculated total mass loss was 62.9%, which is fairly close to that measured (64.63%). So we conclude that the samples are fluoridized completely to MgF_2 in the last two steps.

3.2. The mechanism of MgF_2 formation

CCl_2F_2 is a chemically and thermally stable gas, it does not react with other compounds and does not decompose even at 500 °C in the absence of catalysts. With catalysts, however, including SiO_2/Al_2O_3, mordenite A, mordenite B, zeolite Y, ZrO_2/MoO_3, TiO_2/SiO_2, TiO_2/ZrO_2 [5] and PO_4/ZrO_2 [6] and Al_2O_3/SiO_2 [7], CCl_2F_2 can be decomposed at lower temperatures. Tajima et al. [8] discussed whether H_2O or O_2 is needed for the catalytic decomposition of CCl_2F_2 by thermodynamic calculation. When H_2O participates in the decomposition the products are CO and/or CO_2, HF and HCl. If O_2 is present, the products are CO and/or CO_2, F_2 and Cl_2 at about the same temperature.

In thermal analysis of $MgCl_2·4H_2O$ with CCl_2F_2 as a flowing gas, H_2O was released by dehydration of

Table 2
The thermodynamic data of possible reactions of $MgCl_2$ and Mg(OH)Cl with HF

Name	Reaction	$\Delta H^\circ_{m,298.15\,K}$ (kJ mol^{-1})	$\Delta G^\circ_{m,298.15\,K}$ (kJ mol^{-1})
R1	$MgCl_2 + 2HF \rightarrow MgF_2 + 2HCl$	−121.10	−119.71
R2	$Mg(OH)Cl + 2HF \rightarrow MgF_2 + HCl + H_2O$	−122.46	−112.21

the solid and it can participate in the decomposition of CCl_2F_2 possibly yielding CO and/or CO_2, HF and HCl with the H_2O retained at the surface of $MgCl_2$ and Mg(OH)Cl. In our work, MgF_2 was formed between 252 and 350 °C, which is somewhat higher than 200 °C of the decomposition of CCl_2F_2 with the effective catalyst, TiO_2/SiO_2 [5]. The reactant vessel, Al_2O_3, cannot effectively catalyzed the decomposition without additional SiO_2 [7]. So we can deduce that the $MgCl_2$ and Mg(OH)Cl present catalyze the decomposition of CCl_2F_2 to a mixed gas including HF. This HF further react with $MgCl_2$ and Mg(OH)Cl to form MgF_2.

We have made the thermodynamic calculations for the reactions of $MgCl_2$ and Mg(OH)Cl with HF. The thermodynamic data for the substances involved were obtained from [9]. In Table 2, the possible reactions of $MgCl_2$ and Mg(OH)Cl with HF were shown with their $\Delta H^\circ_{m,298.15\,K}$, $\Delta G^\circ_{m,298.15\,K}$ values, their relations of ΔG°_m versus T calculated by Gibbs–Helmholtz equation in the range of temperature of our experiment is shown in Fig. 2. From the calculations, the reactions R1, R2 are shown to have negative ΔG°_m in the range of temperature of interest here: this means that $MgCl_2$ and MgCl(OH) can react with HF at these temperatures. Since the strength of Mg–O (363.2 ± 12.6 kJ mol^{-1}) is greater than Mg–Cl (327.6 ± 2.1 kJ mol^{-1}) [10], we can conclude that peak δ corresponds $MgCl_2$ reacting with HF and peak ε corresponds to the reaction of Mg(OH)Cl with the gas. Thus, the mechanism could be expressed as follows:

$$CCl_2F_2 + H_2O \xrightarrow{MgCl_2,Mg(OH)Cl,250\,^\circ C} CO + CO_2 + HF + HCl$$

$$MgCl_2 + 2HF \xrightarrow{291\,^\circ C} MgF_2 + 2HCl$$

$$Mg(OH)Cl + 2HF \xrightarrow{316\,^\circ C} MgF_2 + HCl + H_2O$$

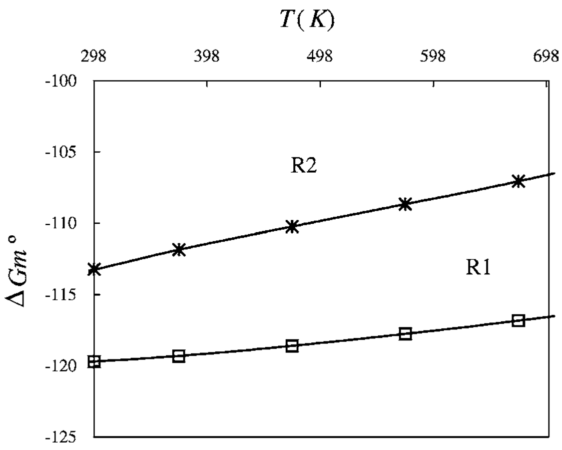


Fig. 2. Plot ΔG°_m vs. T for possible reactions of $MgCl_2$ and Mg(OH)Cl with HF (see Table 2).

3.3. Fluid-bed experimental

The components of the products of the reaction of CCl_2F_2 and $MgCl_2{\cdot}6H_2O$ at different temperatures in the non-isothermal fluid-bed experiment are shown in Table 3. From these results, it is concluded that MgF_2 began to form from 200 °C. This indicates that large gas flow rate can lower the temperature of the reaction in the fluid-bed reactor.

Table 3
Solubility and components of the products in fluid-bed experiment

T (°C)	Solubility in water	Mg/Cl	H_2O (%)	Components of the products
50	+	1/2	54.47	$MgCl_2{\cdot}6.41H_2O$
100	+	1/2	49.58	$MgCl_2{\cdot}5.20H_2O$
150	+	1/2	30.99	$MgCl_2{\cdot}2.37H_2O$
200	−	1/2	14.04	$MgCl_2{\cdot}H_2O + MgF_2$
250	−	1/1.89	5.53	$MgCl_2$ + Mg(OH)Cl + MgF_2
300	−	1/1.36	3.50	$MgCl_2$ + Mg(OH)Cl + MgF_2

Note: (+) represents the sample was completely soluble in water; (−) represents the sample was incompletely soluble in water.

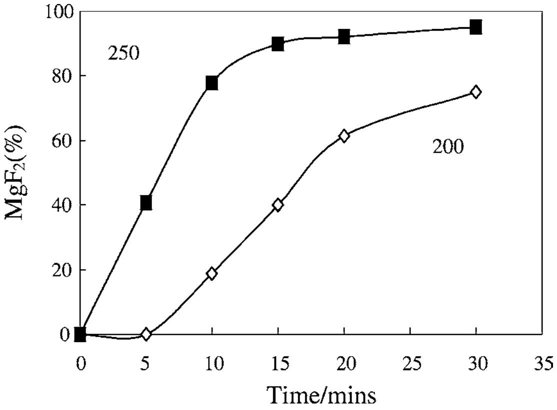


Fig. 3. MgF_2 formed by isothermal reaction of $MgCl_2{\cdot}6H_2O$ with CCl_2F_2 in fluid-bed reactor.

In the isothermal fluid-bed experiment, the percentage of MgF_2, residue in washing with HCl (eq.), of the products at different period of time is shown in Fig. 3. There is evidence that the hydrated magnesium chloride can effectively react with the mixture of CCl_2F_2 and air to form MgF_2 in the fluid-bed reactor, even at CCl_2F_2/air ratios less than 1:10 and the preferable temperature is 250 °C.

The results above suggest that the reaction of our interest can take place across a wide range of CCl_2F_2 concentrations between 200 and 250 °C. The hydrated magnesium chloride can react to form MgF_2 in a short period of time. Because of technical difficulties we did not analyze the gas phase composition after the reaction in the fluid-bed reactor. However, even if the reacted proportion of CCl_2F_2 in the mixed gas is comparatively low, we can deplete the atmosphere-damaging gas completely by circulating it repeatedly in a fluid-bed reactor with renewing magnesium chloride.

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