

## **DESORPTION BEHAVIOUR OF HF, HCFC-133a AND HFC-134a ON A CATALYST SUPPORTED ON $\gamma$ -AlF<sub>3</sub>**

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### **Abstract**

The desorption behaviour (desorption temperature and extent of desorption) of HF, HCFC-133a (CF<sub>3</sub>CH<sub>2</sub>Cl) and HFC-134a (CF<sub>3</sub>CH<sub>2</sub>F) on  $\gamma$ -AlF<sub>3</sub> or catalyst supported on  $\gamma$ -AlF<sub>3</sub> was studied using an adsorption apparatus and TG, DTA and DSC methods. On the basis of the results a reaction mechanism was proposed for the preparation of HFC-134a. The  $\gamma$ -AlF<sub>3</sub> employed for preparing the catalyst was expected to be stable below 550°C based on the crystal-line phase transition temperature of  $\gamma$ -AlF<sub>3</sub>.

**Keywords:** aluminium fluoride, hydrogen fluoride, 1,1,1,2-tetrafluoroethane, 1,1,1-trifluoro-2-chloroethane

### **Introduction**

HFC-134a (CF<sub>3</sub>CH<sub>2</sub>F) has no ozone depletion potential (ODP) and only low global warming potential (GWP) values compared with chlorofluorocarbons (CFCs) due to the replacement of chlorine by fluorine or hydrogen in the molecule [1, 2]. So it is used as a prime substitute of CFC-12. HFC-134a is prepared by heterogeneous catalyzed fluorine/chlorine exchange between chlorinated hydrocarbons and HF. Chromium fluoride is mainly used as catalyst. Several papers have been published about the investigation of the active components and carriers of catalysts [3–7].  $\gamma$ -AlF<sub>3</sub> is one of the few carriers which can be used in vapour-phase catalytic fluorination reactions. The catalyst supported on  $\gamma$ -AlF<sub>3</sub> and promoted by transition metal cations possesses a relatively high catalytic activity and long life in the above reaction [8, 9] and has been employed in industrial process. Despite the importance of catalysts based on AlF<sub>3</sub>, little is known concerning the mechanism of reaction and adsorption of reactants on  $\gamma$ -AlF<sub>3</sub> or

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related catalysts. So we focussed our interest on the investigation of  $\text{AlF}_3$  and the adsorption behaviour of HF, HCFC-133a and HFC-134a on  $\gamma\text{-AlF}_3$  or catalyst. The information obtained can help to judge whether the reaction of the preparation of HCF-134a proceeds according to the Langmuir-Hinshelwood (L-H) mechanism or the Rideal-Eley (R-E) mechanism or neither of them [10, 11]. In the present work (1) the desorption temperature and the extent of desorption HF, HCFC-133a and HFC-134a from  $\gamma\text{-AlF}_3$  or catalyst, and (2) the change in the crystalline phase transition of  $\text{AlF}_3$  with temperature in the range 100–700°C were studied.

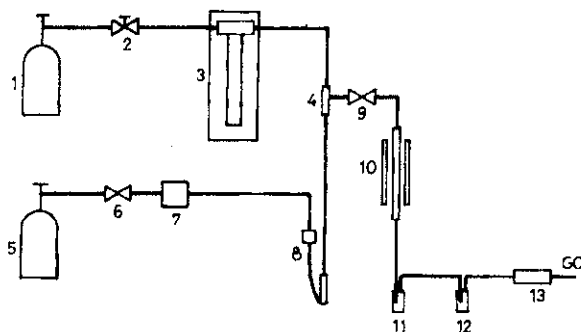
## Experimental

### Materials

Catalyst (surface area  $37.29 \text{ m}^2 \text{ g}^{-1}$ ) supported on  $\gamma\text{-AlF}_3$  and promoted by chromium, cobalt and magnesium salts and  $\gamma\text{-AlF}_3$ , (surface area  $45.79 \text{ m}^2 \text{ g}^{-1}$ , average pore volume  $0.133 \text{ cm}^3 \text{ g}^{-1}$ ), 90%  $\gamma\text{-AlF}_3$  contaminated by 10% amorphous  $\text{AlF}_3$ , were prepared in our laboratory [12]. AHF (99.90% purity) produced by Shan Dong Chemical Co., China and  $\text{N}_2$  (99.5% purity) produced by Xi'an Chemical Reagent Factory were used.

### Equipment and conditions

The apparatus used for measuring the adsorption is depicted in Fig. 1. It consists of a mass flow controller (7) and an AHF flow rate meter (3), an electrically heated tubular nickel reactor (10) (2 cm in diameter and 45 cm in length) equipped with an inside nickel tube ( $\phi 3$ ) for inserting two K type-thermocouples, and GC with TCD.



**Fig. 1** Apparatus for absorption study; 1 – HF; 2, 6, 9 – valve; 3 – HF flow rate meter; 4 – mixture container; 5 – 133a; 7 – mass flow meter; 8 – controller; 10 – reactor; 11 – washing-water; 12 – washing-base; 13 – drier

The sample of  $\gamma$ -AlF<sub>3</sub> or catalyst was packed into the above nickel reactor, dried by heating to 200°C and maintaining at that temperature for 3 h, cooled to room temperature in a N<sub>2</sub> stream (100 ml min<sup>-1</sup>). Then HF was passed through the sample in the reactor at a rate of 100 ml min<sup>-1</sup> for 1 h. The sample was flushed at 100°C with N<sub>2</sub> (100 ml min<sup>-1</sup>) in order to remove HF physically adsorbed on the surface of  $\gamma$ -AlF<sub>3</sub> or catalyst. HF was desorbed by heating at a rate of 10°C min<sup>-1</sup> to a maximum temperature of 450°C and absorbed in water in a container by blowing a small amount of N<sub>2</sub> (10 ml min<sup>-1</sup>). The desorbed HF can be determined by measuring the fluoride concentration in the absorption solution with a fluoride ion-selective electrode. Measurement of the potential, of the electrode permit semi-quantitative determination of the extent of desorption and desorption temperature of HF from  $\gamma$ -AlF<sub>3</sub> or catalyst. The F-concentration was calculated from the Nernst equation.

TPD (Temperature Programmed Desorption) spectra of HCFC-133a and HFC-134a from  $\gamma$ -AlF<sub>3</sub> were obtained with a set of special apparatus. In these experiments, about 30 mg of sample was placed into the stainless steel tube reactor, dried by heating to 300°C and held at that temperature for 3 h and cooled to room temperature in flowing N<sub>2</sub> (100 ml min<sup>-1</sup>). Then HCFC-133a and HFC-134a was passed through the sample in the reactor for 1 h and purged with N<sub>2</sub> to remove the residual gases on the surface of sample. After sufficient flushing, the reactor was enclosed with the tubular furnace and heated at a programmed rate of 20°C min<sup>-1</sup> to a maximum temperature of 400°C. The exit gas from the reactor was conducted to a thermal conductivity detector (TCD) and the desorption signal was recorded with XWT-24 instrument produced by Shang-hai Da Hua Instrument Factory, China.

The desorption of HCFC-133a and HFC-134a from  $\gamma$ -AlF<sub>3</sub> or catalyst was determined by means of TG method with a DuPont 2000 instrument supported by General V 4.1 software. The sample of  $\gamma$ -AlF<sub>3</sub> or catalyst was packed into the stainless steel reactor, dried by heating to 200°C and held at this temperature for 3 h in flowing N<sub>2</sub> and cooled to room temperature. Then HCFC-133a or HFC-134a was passed through the sample in the reactor for 1 h. A small portion of the sample from the above reactor was put into the sample cell of the TG instrument and heated to 100°C and held at that temperature for 1 h in flowing N<sub>2</sub> (30 ml min<sup>-1</sup>) in order to remove physically adsorbed materials. The sample cell was heated at a rate of 20°C min<sup>-1</sup> to a maximum temperature of 400°C to desorb chemical absorbates. The sample mass before and after desorption was recorded.

DTA was employed to determine the heat of desorption of HCFC-133a or HFC-134a from  $\gamma$ -AlF<sub>3</sub>. The  $\gamma$ -AlF<sub>3</sub> (160–180 mesh) was placed in a stainless steel reactor tube ( $\phi$  8), dried by heating from room temperature to 400°C at a rate of 10°C min<sup>-1</sup>, held at that temperature for 10 h, cooled to room temperature. The sample was outgassed at 0.85 kg.f/cm<sup>2</sup>, heated to 400°C and held at that temperature for 1 h, cooled to room temperature and outgassing was stopped. The stream

of HCFC-133a or HFC-134a ( $10 \text{ ml min}^{-1}$ ) was passed through the sample cell for 10 min, then the sample was flushed with  $\text{N}_2$  until the difference thermal signal was stable. Finally it was heated at a rate of  $15^\circ\text{C min}^{-1}$  to  $400^\circ\text{C}$ , while the chemical absorbate was desorbed at a definite temperature. The desorption heat of HCFC-133a or HFC-134a was recorded by the difference thermal signal. The instrument used was a model LCT-1 thermal analyser made in Bei-jing Spectrial Instrument Factory, China.

The crystalline phase transition of  $\text{AlF}_3$  was observed using a Perkin-Elmer model DSC-2. The sample of  $\text{AlF}_3$  was placed into the sample cell, heated to  $100^\circ\text{C}$  and maintained at that temperature for 1 h, and then heated at a rate of  $20^\circ\text{C min}^{-1}$  from 100 to  $700^\circ\text{C}$ .

## Results and discussion

The desorption curves of HF on  $\gamma\text{-AlF}_3$  and catalyst in Figs 2 and 3 shows that HF is adsorbed strongly on  $\gamma\text{-AlF}_3$  and catalyst. The potential change of a fluoride ion-selective electrode in the absorption solution during the process of HF desorption from catalyst and  $\gamma\text{-AlF}_3$  is about 190 and 90 mV, respectively; the desorption temperature of HF is about  $195^\circ\text{C}$  from catalyst and  $125^\circ\text{C}$  from  $\gamma\text{-AlF}_3$ , which indicates that HF is more strongly adsorbed by the catalyst than by  $\gamma\text{-AlF}_3$ , probably due to by  $\text{CrF}_3$  or  $\text{CoF}_2$  present at the surface of the catalyst.

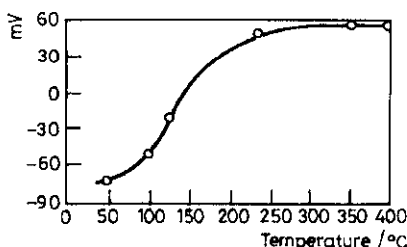


Fig. 2 Desorption of HF on  $\gamma\text{-AlF}_3$

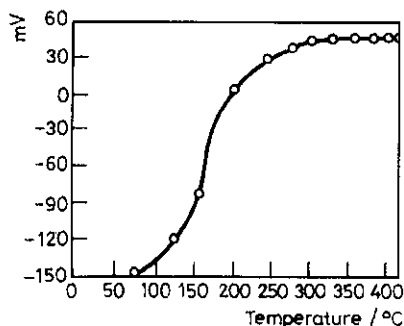


Fig. 3 Desorption curve of HF on catalyst

**Table 1** Experimental results of TG

Experimental	Sample	Conditions of pretreatment	Heating rate	Relative mass of sample/%	
				initial	final difference
Desorption of 133a from $\gamma$ -AlF <sub>3</sub>	17.2770	100°C for 1 h	20	99.35	98.64 0.79
Desorption of 134a from $\gamma$ -AlF <sub>3</sub>	12.9050	100°C for 1 h	20	99.26	98.43 0.83
Desorption of 133a from catalyst	13.4370	100°C for 1 h	20	99.05	97.69 1.36
Desorption of 134a from catalyst	9.9820	100°C for 1 h	20	99.09	97.27 1.72

The results of desorption measurements for HCFC-133a and HFC-134a for  $\gamma\text{-AlF}_3$  and catalyst are listed in Table 1. The results show that the adsorption of HFC-134a is stronger than that of HCFC-133a on the same  $\gamma\text{-AlF}_3$  or catalyst, which may be caused by the fact that the chlorine in  $\text{CF}_3\text{CH}_2\text{Cl}$  is replaced by fluorine, thus the molecular size becomes smaller and a portion of HFC-134a can be adsorbed by small pores of  $\gamma\text{-AlF}_3$  causing an increase in the adsorption capacity for HFC-134a.

Heats of desorption of HCFC-133a and HFC-134a for  $\gamma\text{-AlF}_3$  are shown in Table 2. It can be seen in Table 2 that the heat of desorption of HFC-134a is larger than that of HCFC-133a from  $\gamma\text{-AlF}_3$  or  $\text{Al}_2\text{O}_3(\text{F})$ , the desorption temperature of HFC-134a on  $\gamma\text{-AlF}_3$  (Fig. 4) is  $215^\circ\text{C}$  and that of HCFC-133a is  $200^\circ\text{C}$ , which also indicates that HFC-134a is more strongly adsorbed than HCFC-133a on  $\gamma\text{-AlF}_3$ .

Table 2 Desorption of HCFC-133a and HFC-134a from  $\gamma\text{-AlF}_3$  or  $\gamma\text{-Al}_2\text{O}_3(\text{F})$

Sample	Surface area $\text{m}^2 \text{g}^{-1}$	Heat of desorption $\text{J g}^{-1} \text{cat.}$	
		HCFC-133a	HFC-134a
1.	35	6.18	9.81
2.	86	7.71	26.0

The crystalline phase transition of  $\gamma\text{-AlF}_3$  is shown in Fig. 5. As the DSC curve in Fig. 4 indicates, a crystalline phase transition of  $\text{AlF}_3$  occurs in the range  $100\text{--}280^\circ\text{C}$ , the peak temperature being  $197.71^\circ\text{C}$  which is the point of transformation of hydrated  $\text{AlF}_3$  into  $\gamma\text{-AlF}_3$ , starting from  $109.5^\circ\text{C}$ . The enthalpy of crystalline transition is  $111.17 \text{ J g}^{-1}$ . The other peak at about  $550^\circ\text{C}$  is the transition point of  $\gamma\text{-AlF}_3$  to  $\alpha\text{-AlF}_3$ . The surface area of  $\text{AlF}_3$  and the catalytic activity of the related catalyst decrease remarkably when  $\gamma\text{-AlF}_3$  becomes  $\alpha\text{-AlF}_3$ . Therefore, the reaction of preparation of  $\gamma\text{-AlF}_3$  is strictly controlled below  $400^\circ\text{C}$  since high reaction temperature causes local sintering of  $\gamma\text{-AlF}_3$ . The experimental result shows that  $\gamma\text{-AlF}_3$  is quite stable in the range  $280\text{--}550^\circ\text{C}$ .

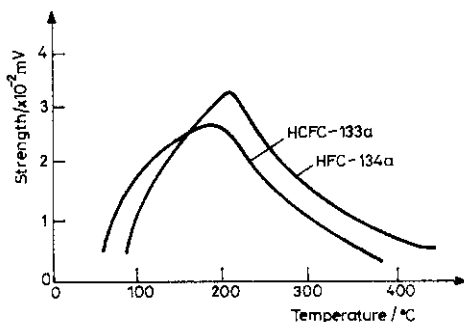


Fig. 4 The curve of HFC-134a TPD on  $\gamma\text{-AlF}_3$

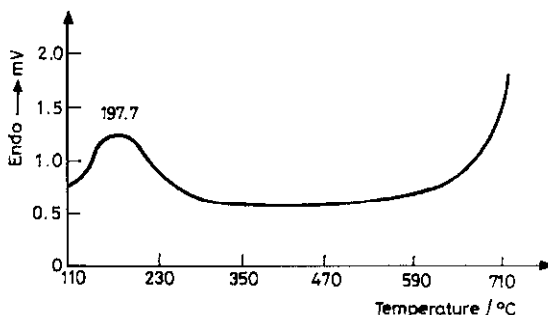


Fig. 5 DSC curve of crystalline phase transition of  $\text{AlF}_3$  at a heating rate of  $20^\circ\text{C}/\text{min}$

The desorption behaviour of HF, HCFC-133a and HFC-134a on  $\gamma\text{-AlF}_3$  or catalyst shows that the desorption temperature is about  $200^\circ\text{C}$  or below. While the reaction temperature of preparation of HFC-134a by reacting HF and HCFC-133a exceeds  $350^\circ\text{C}$ , reactants and products have completely desorbed before attaining the reaction temperature. So the reaction of producing HFC-134a is probably controlled by the kinetics, and not by the adsorption process. Maybe the rate-determining step is a surface reaction.

## Conclusions

a. The temperature of desorption of HF from  $\gamma\text{-AlF}_3$  is about  $125^\circ\text{C}$  and that on a catalyst supported on  $\gamma\text{-AlF}_3$  is about  $200^\circ\text{C}$ , which indicates that the adsorption of HF is much stronger on the catalyst than on  $\gamma\text{-AlF}_3$ .

b. The temperature of desorption of HCFC-133a from  $\gamma\text{-AlF}_3$  is about  $200^\circ\text{C}$ , and that of HFC-134a is about  $215^\circ\text{C}$  which also indicates that HFC-134a is more strongly adsorbed on  $\gamma\text{-AlF}_3$  than HCFC-133a.

c. The study of desorption of HCFC-133a or HFC-134a from  $\gamma\text{-AlF}_3$  or catalyst and the heats of desorption of HCFC-133a and HFC-134a from  $\gamma\text{-AlF}_3$  also led to the same conclusion as b.

d. DSC investigations show that  $\gamma\text{-AlF}_3$  has a good thermal stability in the range  $280\text{--}550^\circ\text{C}$  and it is suitable as carrier to support active components in the above temperature range.

e. The difference in the desorption temperatures is much smaller than that in the reaction temperatures, indicating that the reaction of preparation of HFC-134a does not occur according to the classical reaction mechanisms of L-H or R-E, and a surface reaction is probably the rate-determining step.

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