Synthesis of HFC-134a over CrF_3/AlF_3 catalysts

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The effect of the structure of AlF_3 supports in CrF_3/AlF_3 catalysts and their activity were studied, and a selection of suitable reaction conditions for fluorination of trichloroethylene and HCFC-133a was made. We found that neither AlF_3 (α- and γ-modifications) nor CrF_3/α-AlF_3 exhibits significant activity for the reaction of HF with CCl_2=CHCl or CF_3CH_2Cl. However, CrF_3/γ-AlF_3 exhibits high activity, which increases with increasing surface area and decreasing crystallite size of the γ-AlF_3 support, and that dramatically affects the fluorination of CF_3CH_2Cl. Investigation of a series of CrF_3/γ-AlF_3 catalysts shows that the turnover rates per unit of the total surface area and of the free CrF_3 surface area significantly increase with increasing content of Cr^{3+} loading. Optimum temperature for the reaction of HF with CCl_2=CHCl is 260°C, while with CF_3CH_2Cl it is 350°C, with flow ratios HF : TCE = 6 : 1 and HF : HCFC-133a = 10 : 1.

Keywords: AlF_3 supports; CrF_3/AlF_3 catalyst; activity; reaction conditions

1. Introduction

Synthesis of novel substitutes to replace the ozone depleting chlorofluorocarbons (CFCs) presents a dramatic challenge to process chemists and engineers [1]. 1,1,1,2-tetrafluoroethane (HFC-134a) is generally considered as the first choice of alternatives of two-carbon HFCs and much work has been done for its commercialization, as revealed by numerous patents and literatures [2–6]. Unfortunately, the relevant chemistry has been neglected and there currently exists little guidance for the catalysts design.

The effect of the structure of the AlF_3 support and the content of Cr^{3+} in the CrF_3/AlF_3 catalysts on the activity and selectivity of gas fluorination of trichloroethylene (TCE) to produce HFC-134a were studied, according to the following reactions:

$$\underset{\text{TCE}}{Cl_2C{=}CHCl} + 3HF \rightarrow \underset{\text{HCFC-133a}}{CF_3CH_2Cl} + 2HCl \quad (1)$$

$$CF_3CH_2Cl + HF \rightarrow \underset{\text{HFC-134a}}{CF_3CH_2F} + HCl \quad (2)$$

The performances of the catalyst under various conditions were tested for the catalyst design.

2. Experimental

Apparatus. A nickel reactor (diameter 18 mm) was heated by an electric furnace. The hydrogen fluoride was taken from a cylinder maintained at constant temperature (50°C). The flow regulating system, which consists of a needle valve and flow meter, was kept at 60°C. The needle valve made of 316 stainless steel was used to adjust the flow meter to a desired value. The HF flow meter was calibrated using a fluoride-sensitive lanthanum fluoride electrode. TCE flow rate was controlled by a liquid pump. The HCFC-133a flow rate was controlled by a mass flow meter.

Preparation of catalysts. Various CrF_3/AlF_3 catalysts were prepared by impregnation of a series of AlF_3 with $CrCl_3$ aqueous solution. The catalyst samples were then dried at 120°C under nitrogen, calcined at 350°C, and activated with a nitrogen–hydrogen fluoride mixture at 200–350°C.

Performance of catalysts. After 30 ml of catalysts were activated, the reactor was kept at the desired temperature. HF : HCFC-133a or TCE : HF was allowed to pass the reactor in different experiments. GC-TCD was used to analyze the reaction products which had been previously washed and dried in a series of washing bottles (water and 1 M sodium hydroxide) and drying tube (calcium chloride).

Characterization of catalysts. X-ray diffraction patterns of powder samples were measured on a D/MAX 2400 X-ray diffraction meter using Cu K_α radiation (1.5404 Å). XRD was used to determine the bulk crystalline phase and crystallite sizes of various aluminium fluoride supports. The BET surface areas of a series of AlF_3 were determined by means of low temperature adsorption of nitrogen using a Micromeritics ASAP 2000 apparatus.

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Table 1
The activity of the various catalysts

Catalyst or code [a]	AlF_3			TCE [b] conv. (%)	HCFC-133a sel. (%)	HCFC-133a [c] conv. (%)	HFC-134a sel. (%)
	BET surface ($m^2\ g^{-1}$)	bulk phase	cryst. size (Å)				
AlF_3	26.1	α	229	15.4	87	1.0	61.4
AlF_3	50.4	γ	92.4	35.5	85	3.0	65.2
C-00	26.1	α	229	45.2	88	7.8	71.6
C-01	29.6	γ	164	78.6	95	11.3	98.4
C-11	36.8	γ	135	96.9	99.8	16.2	99.5
C-07	42.0	γ	117	98.5	99.8	19.8	99.5
C-15	50.0	γ	92.3	98.5	99.8	21.8	99.5
C-04	57.0	γ	74.8	99.5	99.9	23.4	99.5

[a] CrF_3/AlF_3 catalyst.
[b] Reaction conditions: TCE : HF = 1 : 6, 260°C.
[c] Reaction conditions: HCFC-133a : HF = 1 : 10, 350°C.

3. Results and discussion

3.1. The structure of AlF_3 support and the activity of the CrF_3/AlF_3 catalysts

The activity and selectivity of various catalysts for the synthesis of HCFC-133a and HFC-134a are listed in table 1.

Table 1 shows that AlF_3 (γ- and α-modifications) and CrF_3/α-AlF_3 do not exhibit significant activity for reactions (1) and (2). However, CrF_3/γ-AlF_3 does exhibit high activity. The catalytic activity increases with increasing surface area and decreasing crystallite size of the AlF_3 support. The bulk phase and BET surface areas of the AlF_3 supports dramatically affect the fluorination activity of reaction (2). The different activity of the catalysts is due to the structure of their α- and γ-AlF_3 supports. The stable α-AlF_3 is a rhombohedral cell where the aluminum atom is coordinated to six equivalent fluoride ions [7] to form a regular crystal structure which would not exhibit a large surface area. Crystallite sintering at the high preparative temperatures would also favor the formation of large crystallites. A Cr^{3+} catalyst supported by α-AlF_3 with small surface area and large crystallite size is catalytically inactive. However, the metastable γ-AlF_3 is a tetragonal cell where the aluminum atom is coordinated to three kinds of fluoride ions [7]. γ-AlF_3 possesses an open structure and vacancies [8], and, therefore, exhibits a large surface area. The crystallite size of γ-AlF_3 is smaller than that of α-AlF_3, thus the γ-AlF_3 supported Cr^{3+} catalyst exhibits high activity for halogen exchange reactions. Our results indicate that the halogen exchange reaction (2) is more difficult than reaction (1), conforming to the thermodynamic prediction.

3.2. Various contents of Cr^{3+} in CrF_3/γ-AlF_3 catalysts and their activity for reaction (2)

The effects of varying the Cr^{3+} content in CrF_3/γ-AlF_3 catalysts for synthesis of HFC-134a are listed in table 2.

A tendency of increasing of the catalyst surface area with increasing Cr^{3+} content clearly shows that the increasing surface area of the catalyst is to be attributed to the Cr^{3+} in the catalyst. We also measure that γ-AlF_3, used as support in table 2, possesses a surface area of

Table 2
Effect on catalytic activity of varying the Cr^{3+} content [a]

Sample I.D.	Content of Cr^{3+} (%)	$S_{cat.}$ ($m^2\ g_{cat}^{-1}$)	S_{CrF_3} ($m^2\ g_{cat}^{-1}$)	HCFC-133a conv. (%)	Turnover rates per unit of surface ($\mu mol\ m^{-2}\ s^{-1}$)		HFC-134a sel. (%)
					$S_{cat.}$	S_{CrF_3}	
SCC-1	0.01	31.1	–	1.2	0.37×10^{-3}	–	90.9
SCC-2	0.02	35.0	3.5	2.3	0.63×10^{-3}	6.27×10^{-3}	90.9
SCC-3	0.48	43.8	12.3	5.7	1.24×10^{-3}	4.42×10^{-3}	96.9
SCC-4	0.92	46.8	15.3	8.1	1.65×10^{-3}	5.05×10^{-3}	98.8
SCC-5	4.57	52.8	21.3	15.8	2.85×10^{-3}	7.06×10^{-3}	99.2
SCC-6	6.46	53.2	21.7	19.4	3.48×10^{-3}	8.53×10^{-3}	99.4
SCC-7	8.46	54.1	22.6	22.6	3.98×10^{-3}	9.54×10^{-3}	99.5

[a] Reaction conditions: HCFC-133a : HF = 1 : 10, 350°C. The weight of the catalyst is 23.4 g.

Table 3
The effect of temperature on the reaction of TCE with HF [a]

Temp. (°C)	TCE conv. (%)	Rate [b] (μmol ml^{-1} s^{-1})	HCFC-133a sel. (%)
240	86	1.06	99.9
260	98	1.21	99.6
280	99	1.22	99.4
300	100	1.24	98.0
320	100	1.24	96.0

[a] CrF_3/γ-AlF_3 catalyst: content of 5% Cr^{3+}, γ-AlF_3 (surface area 50.0 m^2 g^{-1}).
[b] μmol HCFC-133a converted ml^{-1} s^{-1}.

Table 5
HCFC-133a reaction with HF at various temperatures

Temp. (°C)	HCFC-133a conv. (%)	Rate [a] (μmol ml^{-1} s^{-1})	HFC-134a sel. (%)
260	0.5	3.7×10^{-3}	100
280	1.0	7.4×10^{-3}	100
300	3.2	23.4×10^{-3}	99.96
325	10.3	76.6×10^{-3}	99.7
350	21.0	156.3×10^{-3}	99.5
375	26.2	194.9×10^{-3}	98.5
400	29.5	219.5×10^{-3}	96.3

[a] μmol HCFC-133a converted ml^{-1} s^{-1}.

31.5 m^2 g^{-1} under the reaction conditions instead of 42.3 m^2 g^{-1} before reaction. With these data, we can roughly estimate a free CrF_3 surface area by subtracting the surface area of the γ-AlF_3 support (31.5 m^2 g^{-1}) from that of the catalysts. Both the turnover rate per unit of the total surface area of the catalyst and that of the free CrF_3 surface area were obtained by calculation, the former is more exact than the latter, but the latter yields comprehensible information about the active compound. Moreover, both turnover rates are increased with increasing the Cr^{3+} content in the catalysts.

3.3. Selection of optimum conditions for reactions (1) and (2)

Selection of reaction conditions for reaction (1)

The activities for the reaction of TCE with HF at various temperatures and a flow ratio of TCE : HF = 50 : 600 (1 : 6) are listed in table 3.

The activity for reaction (1) increases with increasing temperature. At 260–280°C, the catalyst exhibits its highest selectivity with good conversion. Above 280°C, reaction selectivity is reduced by unwanted by-products.

Selection of reaction conditions for reaction (2)

The performance of the CrF_3/γ-AlF_3 (5% Cr^{3+}, γ-AlF_3 surface area 50.0 m^2 g^{-1}) for synthesis of HFC-134a under various reaction conditions is listed in tables 4, 5 and 6. The results indicate that a flow ratio of HF : HCFC-133a = 10 : 1 is suitable for reaction (2); at such a flow ratio, the activity for synthesis of HFC-134a is the highest, and the selectivity to HFC-134a is 99.5%.

The results indicate that the conversion of HCFC-133a increases with increasing reaction temperature, while the selectivity to HFC-134a decreases with the temperature at a flow ratio of HF : HCFC-133a = 300 : 30. At 350°C, the catalyst exhibits high activity and selectivity. This finding confirms that reaction (2) needs a higher temperature than reaction (1). This result provides further evidence that halogen exchange by reaction (2) is more difficult than by reaction (1). The Arrhenius activation energy of the reaction of HCFC-133a with HF was measured by using the well-known method of measuring the variation of initial rates as a function of temperature. During these measurements, the HF : HCFC-133a reactant ratio was maintained at the constant value of 300 : 30 and the %conversions of HCFC-133a were kept at values at or below 10%. Fig. 1 is an Arrhenius plot for the reaction of HCFC-133a with HF, from which a value of 161.5 kJ mol^{-1} is achieved as the activation energy.

Table 6 shows that the activity for reaction (2) decreases with decreasing contact time, selectivity to HFC-134a does not change at varying contact time, the rates of reaction (2) and yields of HFC-134a increase with increasing SV. Requiring the catalyst to provide certain activity and yields, selection of a space velocity of over 660 h^{-1}, and yields of HFC-134a of more than 57.2 g h^{-1} ℓ^{-1} is suitable for reaction (2).

Table 4
The effect of flow ratio of HF : HCFC-133a on the catalytic reaction of HCFC-133a with HF

HF : HCFC-133a (ml : ml)	Contact time (s)	HCFC-133a conv. (%)	Rate [a] (μmol ml^{-1} s^{-1})	HFC-134a sel. (%)
50 : 10	30.0	27.5	68.2×10^{-3}	98.5
100 : 10	16.0	30.1	74.7×10^{-3}	99.5
200 : 10	8.5	28.2	69.9×10^{-3}	99.5
300 : 10	5.6	26.2	65.0×10^{-3}	99.5

[a] μmol HCFC-133a converted ml^{-1} s^{-1}.

Table 6
The effect of space velocity on the HCFC-133a reaction with HF

HF : HCFC-133a (ml : ml)	SV (h^{-1})	Contact time (s)	HCFC-133a conv. (%)	Rate[a] (μmol ml^{-1} s^{-1})	HFC-134a sel. (%)	Yield ($g\,\ell^{-1}\,h^{-1}$)
100 : 10	220	16.4	30.1	75×10^{-3}	99.5	27.2
200 : 20	440	8.2	23.1	116×10^{-3}	99.5	46.9
300 : 30	660	5.3	21.0	156×10^{-3}	99.5	57.2
400 : 40	880	4.2	18.9	187×10^{-3}	99.5	68.5
500 : 50	1100	3.3	18.0	223×10^{-3}	99.5	81.6

[a] μmol HCFC-133a converted ml^{-1} s^{-1}.

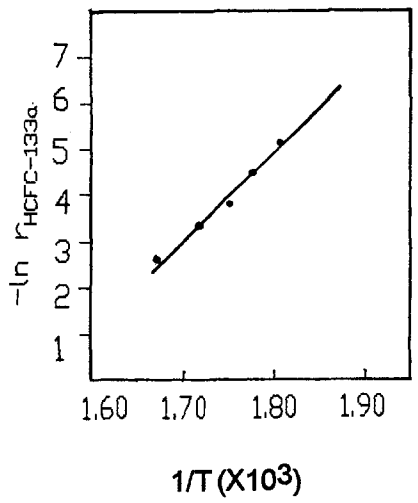

Fig. 1. Arrhenius plot for the reaction of HCFC-133a with HF to form HFC-134a.

4. Conclusions

This study shows that the activity of halogen exchange via reactions (1) and (2) increases with increasing surface areas and decreasing crystallite sizes of the γ-AlF_3 supports in CrF_3/AlF_3 catalysts which, in turn, dramatically affect the fluorination of reaction (2). The turnover rate per unit of CrF_3 surface area is found to be a function of the Cr^{3+} content. The optimum conditions for the two-step gas phase catalytic process are a temperature of 260°C for reaction (1) and a temperature of 350°C with a flow ratio of HF : HCFC-133a = 10 : 1 for reaction (2).

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