

CATALYTIC FLUORINATION OF HCFC-133a (1,1,1-TRIFLUORO-2-CHLOROETHANE)

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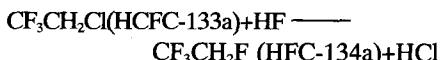
Abstract – Catalytic fluorination of HCFC-133a was performed over metal oxide catalysts. Chromium oxide showed the best catalytic activity among several metal oxides tested. An increase in the crystallinity with decreased surface area resulted in a decrease of catalytic activity for the fluorination reaction. Active phase of chromia is Cr-O-F-OH having a proper ratio of O/F and a high hydroxyl content. The hydroxyl content on the catalyst is strongly dependent on support material. The selectivity to HFC-134a is independent of the O/F ratio on the Cr surface.

Key words: Chromium Oxide, Fluorination, 1,1,1-Trifluoro-2-Chloroethane, 1,1,1,2-Tetrafluoroethane

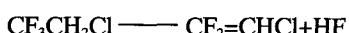
INTRODUCTION

Recent scientific studies have shown a relation between stratosphere ozone depletion and chlorofluorocarbon (CFC) emission [Molina, 1974]. In 1990 the Montreal Protocol, an international agreement regarding CFC production and use, have required a phaseout of CFC production by 1996 in developed countries and by 2006 year in developing countries. As CFC is so important to many aspects of modern society, many countries made an effort to substitute CFC. Selected by industry are candidates, such as hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). They have low ozone depletion potential (ODP) and global warming potential (GWP) values due to the absence of chlorine and presence of hydrogen in the molecule. Significant research and development programs are underway to commercialize them.

In CFC substitutes, HFC-134a (1,1,1,2-tetrafluoroethane) has zero ozone depletion potential and is a prime candidate for the replacement of CF_2Cl_2 in refrigerate systems, medical aerosols, and some foam blowing application. Therefore, many routes of producing HFC-134a have been developed [Bell, 1978; Potter, 1979; Scherer et al., 1973; Soboley, 1988]. One of popular methods is fluorination of HCFC-133a (1,1,1-trifluoro-2-chloroethane) using chromium oxide or supported metal catalysts [Brunet et al., 1995; Kim et al., 1993; Lee et al., 1997; Lu et al., 1996]. The reaction involved is



with



as a main by-product. It is difficult to exchange the halogen

(F,Cl) due to equilibrium restriction. With stoichiometric quantities of reagents and operating above 350 °C, only about 3 % conversion of HFC-134a is obtained. Forcing condition and the use of a large excess of HF are required to shift the equilibrium in the desired direction [Manzer et al., 1993].

We have focused our study on the gas-phase catalytic fluorination of HCFC-133a (1,1,1-trifluoro-2-chloroethane) with HF and this paper presents the results of activity test over metal oxides, and supported and unsupported chromium oxides. The results correlated with the phase composition on the surface in order to find phase composition of catalytically active sites.

EXPERIMENTAL

1. Preparation of Catalysts

The catalyst of chromia used in this paper as starting material was hydrogel prepared by precipitation method. The chromium hydroxide was prepared by adding a solution of ammonia at a constant rate to a solution of chrome nitrate. The final pH was set equal to 7.0 and the hydroxide formed was kept constantly stirred so as to complete the precipitation. It was then filtered and washed several times with distilled water and dried in an oven at 135 °C for 12 h. Supported metal oxide was prepared by the precipitation method followed by washing, drying and calcination at 450 °C for 4 h.

2. Fluorination Reaction

Fluorination of HCFC-133a was carried out at 370 °C under atmospheric pressure in a fixed-bed reactor. The reactor was made of inconel and heated in a furnace. One gram of catalyst was packed in the reactor. Hydrogen fluoride and HCFC-133a as reactants were mixed and diluted in helium using mass flow controllers. The mole ratio of HF/He/HCFC-133a was controlled at 8/5/1 during the reaction. The mixed reactants were fed to the reactor at a rate of 30 ml/min.

The gas products were analyzed by a gas chromatograph

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with a porapak T column (80/100 mesh, 150 cm) and a thermal conductivity detector. The exit gas has been previously washed using a bed of sodium hydroxide and dried using calcium chloride. The conversion of HCFC-133a and the selectivity to HFC-134a ($\text{CF}_3\text{CH}_2\text{F}$) are defined as follows;

$$\text{Conversion of HCFC-133a (\%)} = \frac{(\text{HCFC-133a})_{\text{inlet}} - (\text{HCFC-133a})_{\text{outlet}}}{(\text{HCFC-133a})_{\text{inlet}}} \times 100$$

$$\text{Selectivity toward HFC-134a (\%)} = \frac{(\text{HFC-134a})_{\text{outlet}}}{(\text{HFC-134a})_{\text{outlet}} + (\text{Byproduct})_{\text{outlet}}} \times 100$$

where the subscripts 'inlet' and 'outlet' represent the reactor input and output, respectively.

RESULTS AND DISCUSSION

1. Activity Tests of Various Metal Oxides Supported on AlF_3

Table 1 shows the results on catalytic activity over several metal oxides supported on AlF_3 . The last column in Table 1 represents the bond strength ratio of metal-fluorine to metal-oxygen. The conversion and selectivity are strongly dependent on the bond strength ratio of metal-fluorine to metal-oxygen. A measurable amount of conversion was observed for Ni, Co, Mn, and Cr oxide, whereas almost zero conversion was observed for Ca, Sn and Ce oxide. For metal oxide like

Table 1. Catalytic activity of supported metal oxide for fluorination reaction
(reaction temperature 370 °C, WHSV=1,800 l/kg_{cat} h)

Catalyst	Conversion (%)	HFC-134a selectivity (%)	Bond
10 % CaO/AlF_3	0.0	0.0	1.311
5 % NiO/AlF_3	3.8	81.6	1.139
5 % CoO/AlF_3	8.0	10.0	1.131
10 % MnO/AlF_3	4.0	9.6	1.051
10 % CrO/AlF_3	9.8	95.3	1.036
10 % SnO/AlF_3	0.0	0.0	0.877
10 % CeO/AlF_3	0.0	0.0	0.732

*The ratio of bond strength of metal-fluorine and metal-oxygen.

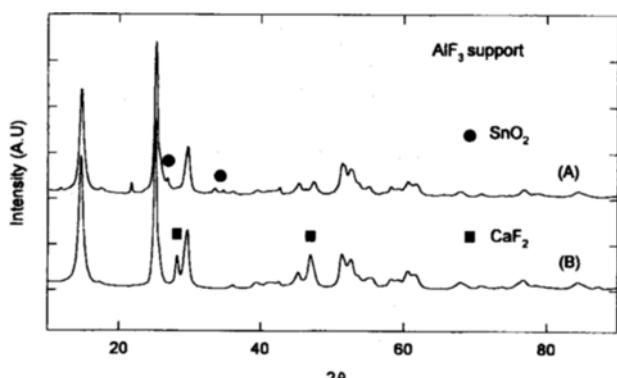


Fig. 1. XRD analyses of metal oxide supported on AlF_3 after reaction test.

A: $\text{SnO}_2/\text{AlF}_3$, B: CaO/AlF_3

CaO which has a strong metal-fluorine bond than metal-oxygen (with the bond strength ratio 1.311), it will be easily transformed into metalfluoride (CaF_2) during the fluorination reaction. On the contrary metal oxides like Sn, Ce will remain as oxide form at the reaction condition since these metal have stronger metal-oxygen bond than metal-fluorine. This was confirmed by XRD results in Fig. 1. It can be established that metal oxides having moderate values of the bond strength ratio (in the range of 1.0-1.2) are catalytically active and these active catalyst may exist as a form of metaloxyfluoride. The results support the report that metaloxyfluoride was an active form for the fluorination reaction [Ruh et al., 1956; Scherer et al., 1975]. Unfortunately the phase of metaloxyfluoride can not be confirmed by XRD probably because it exists as an amorphous phase. Concerning the selectivity to HFC-134a, the bond strength ratio did not give a good correlation. Both Ni and Cr with a high end and low end value in the bond strength ratio, respectively showed high selectivity values, indicating that the degree of fluorination is not an important factor governing the selectivity. From the activity tests, it is found that Cr is best catalyst.

2. Fluorination of HCFC-133a over Supported Cr

In order to find a proper support for the selected Cr catalyst, several supports were tested for the fluorination. Results of the reaction tests are summarized in Table 2. The conversion was decreased in the order of $\text{MgO} > \text{Al}_2\text{O}_3 > \text{TiO}_2$. Almost zero conversion was observed for ZrO_2 . An increase in the reaction temperature enhanced the conversion of HCFC-133a while the selectivity to HFC-134a stayed almost constant. Therefore the yield of HFC-134a can be enhanced by simply increasing the reaction temperature.

Fig. 2 shows TPD (temperature programmed desorption) profiles obtained during the temperature sweeping from 100 °C to 900 °C. The sample was heated in a quartz microreactor at a heating rate of 10 °C/min in flowing He. Desorbed water was detected by a thermal conductivity detector. The amount of desorbed water that was observed at temperatures above 400 °C decreases in the order of $\text{MgO} > \text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{ZrO}_2$. Chromia supported on ZrO_2 shows negligible amount of desorption over a full range of temperature. It coincides with zero conversion for the fluorination reaction. The results in Fig. 2 and Table 2 establish that the larger the amount of water desorbed during the TPD, the higher the conversion during the reaction. Therefore, it is believed that the presence

Table 2. Conversion of HCFC-133a and selectivity of HFC-134a for chromium oxide supported on various metal oxide
(HF/HCFC-133a feed ratio of 8.0, WHSV=1,800 l/kg_{cat} h)

Catalyst	Temperature (°C)							
	320	350	370	400	Conv.	Selec.	Conv.	Selec.
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
CrO/MgO	9.8	98.4	21.4	98.9	25.9	98.8	29.5	97.8
$\text{CrO}/\text{Al}_2\text{O}_3$	4.5	98.0	10.5	97.0	17.3	96.2	22.1	95.0
CrO/TiO_2	-	-	-	-	12.0	94.2	-	-
CrO/ZrO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

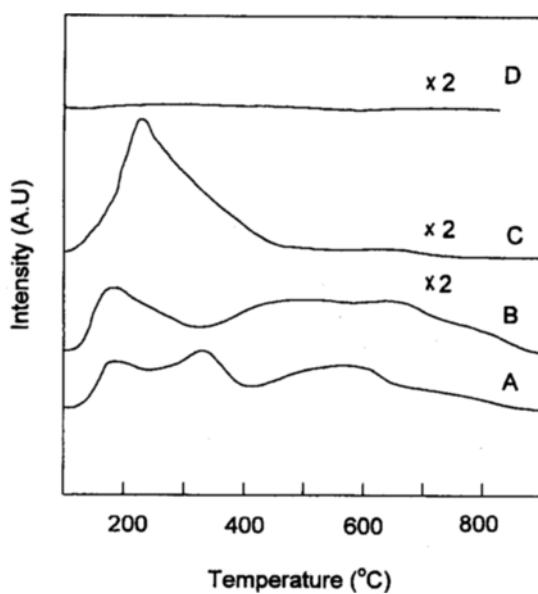


Fig. 2. TPD profile for supported chromium oxide.
A: CrO_x/MgO, B: CrO_x/Al₂O₃, C: CrO_x/TiO₂, D: CrO_x/ZrO

of surface hydroxyl group on the support promotes the catalytic activity of CrO_x supported on metal oxide.

For chromium oxide supported on MgO, the effect of chromium oxide loading on the conversion of HCFC-133a and the selectivity to HFC-134a are shown in Fig. 3. As the chromium oxide content increases from 5 to 10 %, both the conversion and selectivity are increased. Above 10 % chromium content, the conversion and selectivity remains almost the same. The results show that catalytically active phase is Cr, not the support.

3. Effect of Calcination of CrF₃ on Catalytic Activity

Incorporation of oxygen to the CrF₃ structure was attempted in order to confirm that metaloxylfluoride form is an active phase for the fluorination reaction. In order to transform CrF₃ into various forms of CrOxF_y, one gram of CrF₃·4H₂O

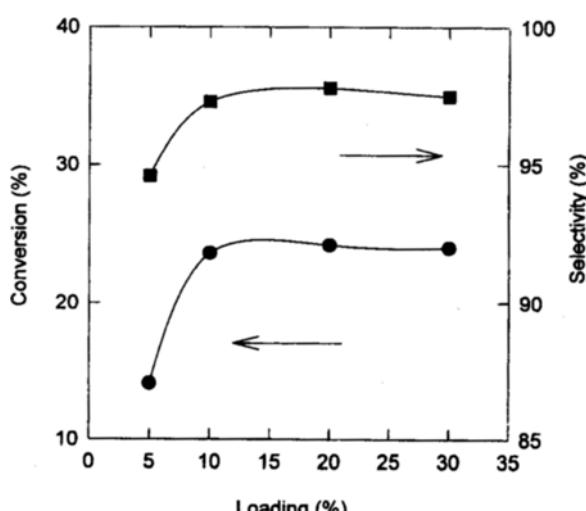


Fig. 3. Effect of Cr loading supported on MgO.
(reaction temperature: 370 °C, WHSV=1,800 l/kg_{cat} h)

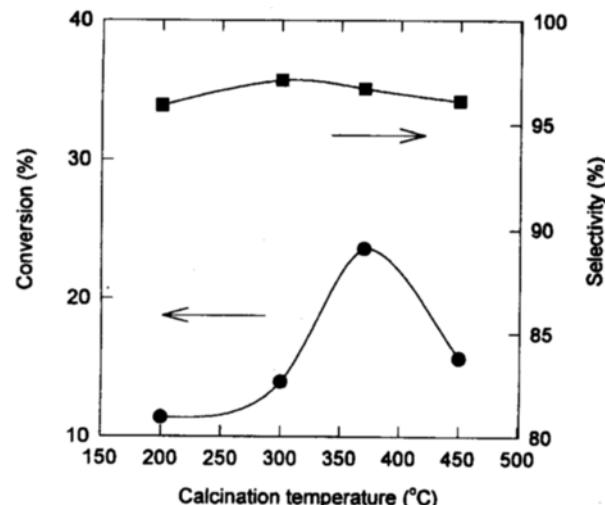


Fig. 4. Effect of calcination temperature of CrF₃·4H₂O in the fluorination reaction.
(reaction temperature: 370 °C, WHSV= 1,800 l/kg_{cat} h)

(Aldrich) was loaded into the reactor and calcined in-situ for 4 h in an air flow of 30 ml/min at 200, 300, 370 and 450 °C, respectively. The fluorination reaction of HCFC-133a was performed at 370 °C.

Fig. 4 presents the effect of calcination temperature on the fluorination of HCFC-133a. The conversion of HCFC-133a shows a maximum at the calcination temperature of 370 °C. Either fluorine rich phase obtained by a high temperature calcination or oxygen rich phase by a low temperature calcination exhibits very low conversion. Therefore, keeping proper ratio of fluorine to oxygen is necessary for obtaining a high conversion. In contrast to the conversion, the selectivity of HFC-134a remains almost constant as a function of the calcination temperature, indicating that fluorine/oxygen ratio on the metal surface is not governing factor for controlling the selectivity.

4. Fluorination of HCFC-133a over Pure Chromium Oxide Catalysts

Chromia having different structure were prepared by the following methods, as it has been known that the structure of chromia depends on treatment method [Macdaniel et al., 1975].

Sample A: The original precipitated hydrogel in the experimental section was heated in flowing hydrogen to 304 °C and held at that temperature for 4 h. The hydrogen was replaced by helium and the temperature was increased to 423 °C and held at that temperature for another 4 h.

Sample B: The original sample was heated in flowing helium at 400 °C for 4 h.

Sample C: The original sample was heated in flowing helium at 800 °C for 4 h.

The color of the sample varied from dark to green with increasing pretreatment temperature.

Sample D: Commercial chromia (from Aldrich)

Results of the reaction test for the four samples are presented in Table 3. The main reaction product is HFC-134a (CF₃CH₂F) which is formed by the halogen exchange reac-

Table 3. Catalytic activity of chromium oxide for fluorination reaction

Catalyst	Surface area (m ² /g)	Conversion (%)	Selectivity (%)	
			HFC-134a	CF ₂ CHCl
A	162	24.4	97.5	0.7
B	80	15.8	96.8	1.4
C	20	6.1	93.1	5.1
D	7	0.0	0.0	0.0

tion between HCFC-133a and HF. Also a little amount of CF₂CHCl as a by-product is produced by dehydrofluorination of HCFC-133a even in the presence of HF. With an increase in the conversion, the selectivity to HFC-134a increased while the selectivity to CF₂CHCl decreased in the order of sample A > B > C.

Fig. 5 shows XRD patterns and their peaks corresponded to the morphology of α -Cr₂O₃. Sample C that has been prepared at higher temperature shows a sharper X-ray lines than sample B. Sample A is X-ray amorphous due to the lack of any long range ordering of the constituents. From the XRD results, we can found that the crystallinity of samples increase in the order of sample A < B < C < D.

The BET surface area are shown in Table 3. Comparing the sample B and C which were pretreated with the same gas helium, the area decreases with increased pretreatment temperature. However, the sample A which experienced higher temperature than the sample B yields higher specific surface area, due to different prehistory during the pretreatment.

The results in Table 3 and Fig. 5 indicate that the increase in the crystallinity of chromium oxide results in a drastic decrease in the surface area of chromium oxide and corresponding decrease in the conversion for the fluorination reaction. The observation of zero conversion with well crystallized commercial Cr₂O₃ (Aldrich) (The sample is known to be treated at temperature above 1,200 °C), implies that crystalline phase shows no activity. Therefore, amorphous phase is considered to be an active phase for the reaction. Burwell et al. [1969] have reported that the surface hydroxyl group on the chromia decreased as the pretreatment-temperature increased. It is also known that amorphous chromia has more surface hydroxyl group than crystalline chromia [Schraml-Marsh et al.,

1992]. Therefore, it can be inferred that the surface hydroxyl group of sample decrease in the order of A > B > C > D. This implies that the existence of the surface hydroxyl group is an important factor for the fluorination reaction. Together with our previous results obtained with Cr on various supports, it can be established that amorphous chromium hydroxide is fluorinated to form an active phase of Cr-O-F-OH compound for the reaction. Keeping a high hydroxyl content with a balanced ratio of oxygen to fluoride content is a key factor for obtaining a high conversion. The selectivity to HFC-134a is decreased with a decrease of amorphous phase (decrease in the hydroxyl content). At present, it is not clear why reduced hydroxyl content promotes the dehydrofluorination reaction of HCFC-133a to CF₂CHCl.

CONCLUSION

Among several metal oxides tested, catalysts having the bond strength ratio of metal-fluorine to metal-oxygen between 1.0 and 1.2 exhibited catalytic activity for the reaction, indicating to us that metaloxyfluoride is an active site for the fluorination reaction. Chromium oxide showed the best catalytic activity. Active phase of chromia is Cr-O-F-OH having a proper ratio of O/F and a high hydroxyl content. The hydroxyl content on the catalyst is strongly dependent on support material. The selectivity to HFC-134a is independent of the O/F ratio on the Cr surface. Decreased hydroxyl content results in a slight decrease in the selectivity to HFC-134a.

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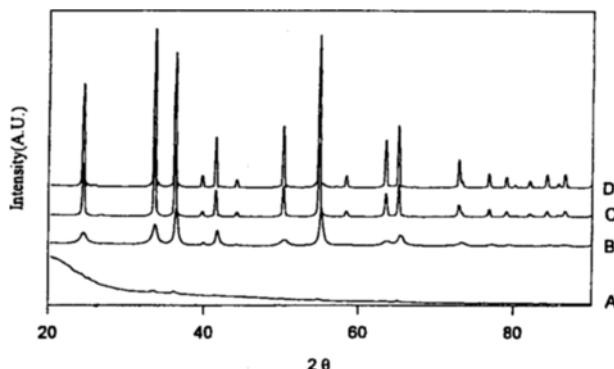


Fig. 5. XRD analyses for pure chromium oxide.
(A: sample A, B: sample B, C: sample C, D: sample D)

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