Preparation of 1,1,1,2-tetrafluoroethane by catalytic fluorination of 1,1,1-trifluoro-2-chloroethane over CrF_3/MgF_2-AlF_3

Hyunjoo Lee, Hoon Sik Kim *, Honggon Kim, Woo Sik Jeong, Inseok Seo

Korea Institute of Science and Technology, CFC Alternatives Research Center, P.O. Box 131 Cheongryang, Seoul 130-650, South Korea

Abstract

The heterogeneous fluorination reactions of CF_3CH_2Cl were performed over CrF_3 supported on MgF_2–AlF_3 and the catalytic activities were compared with those of single support catalysts, CrF_3/MgF_2 and CrF_3/AlF_3, in order to see any enhancing effect of the mixed support on the catalytic activity. The catalytic activities of CrF_3/MgF_2–AlF_3 catalysts were considerably low compared to those of single support catalysts, CrF_3/MgF_2 and CrF_3/AlF_3, indicating the existence of an antisynergy between MgF_2 and AlF_3. XRD measurements show that such an antisynergy effect is mostly attributed to the formation of $MgAlF_5 \cdot 1.5H_2O$ which seems ineffective as a supporting material. The observation of β-AlF_3 in the XRD patterns of the aluminum-rich ($Al/Mg > 1$) catalysts implies that $MgAlF_5 \cdot 1.5H_2O$ or MgF_2 might be responsible for the transformation of γ-AlF_3 into β-AlF_3. FT-IR studies reveal that the fluorination activity is highly dependent on the strength of Lewis and Brønsted acidities on the catalyst. The IR spectra of adsorbed CF_3CH_2Cl show that the intensities of adsorption bands of CF_3CH_2Cl diminish as the amount of $MgAlF_5 \cdot 1.5H_2O$ in the catalyst support increases. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

CF_3CH_2F (HFC-134a) has been considered as an alternative of CF_2Cl_2 (CFC-12) which is responsible for the depletion of stratospheric ozone layer. Chromium fluoride catalysts supported on magnesium fluoride or aluminum fluoride are known to be active and selective catalysts for the preparation of CF_3CH_2F and other hydrofluorocarbons and HCFC [1–6].

Presently, we are studying a fluorination reaction to convert CF_3CH_2Cl (HCFC-133a) to CF_3CH_2F (HFC-134a) using supported chromium fluoride based catalysts. In a previous paper, we reported that the fluorination activity of CrF_3 is remarkably enhanced by the use of MgF_2 as a support [7]. Since it has been proposed that the fluorination and disproportionation catalysts must possess Lewis acidity to account for their activities, one might expect that the performances of CrF_3/MgF_2 catalyst would be improved by adding strongly Lewis acidic AlF_3 [8]. Furthermore, chromium–mag-

* Corresponding author. Tel.: +82-02-958-5855; fax: +82-02-958-5809. e-mail: khs@kistmail.kist.re.kr

nesium–aluminum catalyst is known to possess a better thermochemical strength and a higher activity in comparison with other chromium containing systems such as chromium–aluminum and chromium–magnesium [9]. Surprisingly, however, we found that the catalytic activity of CrF_3/MgF_2 catalyst was significantly reduced by the addition of AlF_3. Likewise, the activity of CrF_3/AlF_3 catalyst was also found to decrease when MgF_2 was used as a co-support with AlF_3. In other word, antisynergy effect was observed in the fluorination of CF_3CH_2Cl over the mixed support catalyst, $CrF_3/MgF_2–AlF_3$, compared to the single component support catalyst, CrF_3/MgF_2 or CrF_3/AlF_3. XRD diffraction measurements were performed to determine the crystalline phases and also to detect phase modifications or formations of new compounds.

In this study, we report some of our results on the investigations on the antisynergy effect of the mixed support, $MgF_2–AlF_3$ on the activity of CrF_3 catalysts by characterizing the structure of the catalysts using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR).

2. Experimental

2.1. Preparation of catalysts

2.1.1. Chemicals

Reagent grade CrO_3, MgO and $AlCl_3 \cdot 6H_2O$ were commercially purchased from Aldrich Chemical CF_3CH_2Cl and anhydrous HF were obtained from PCR and Ulsan Chemical, respectively. All the chemicals were used as received without further purification. $Cr(OH)_3 \cdot xH_2O$ was prepared according to the literature procedure [10]. $CrF_3 \cdot xH_2O$, MgF_2 and AlF_3 were synthesized from $Cr(OH)_3 \cdot xH_2O$, MgO and $AlCl_3 \cdot 6H_2O$, respectively, by reacting with 50% HF.

2.1.2. Synthesis of $CrF_3/MgF_2–AlF_3$ catalyst

50% HF was slowly added to a well-stirred aqueous slurry solution of $Cr(OH)_3 \cdot xH_2O$, MgO and $AlCl_3 \cdot 6H_2O$ for 2 h. Then, the solution was allowed to stand for about 2 h. The resulting precipitates were separated from the mother liquor, washed with H_2O and dried at 140°C overnight. The dried solid was powdered and formed into cylindrical pellets.

2.1.3. Catalyst activation

The prepared catalysts, prior to use, were subject to the activation process which provides them with an activity for the fluorination of CF_3CH_2Cl. 30 g of pelletized catalyst was loaded into the Inconel 600 reactor of 1 in. in diameter and 30 cm long equipped with an electrical heater. The catalyst was dried in-situ at 420°C for 1 h in He at a flow rate of 200 ml/min and was fluorinated by 400 ml/min of HF at 200°C for 2 h, then 400°C for 1 h.

2.1.4. Fluorination reaction

The fluorination reactions were carried out in a fixed bed reactor under an atmospheric pressure. Effluent reaction mixture was analyzed by on-line Gow-Mac 580P TCD gas chromatography equipped with 6 ft Porapak N column after being scrubbed with H_2O and dried over molecular sieve 4A. Flow rates of CF_3CH_2Cl and HF preheated in a chamber at 40°C were carefully controlled by using Matheson mass flow controllers. The molar ratio of $HF/CF_3CH_2Cl = 8$ and the contact time of 6 s were maintained throughout the reaction.

2.2. Characterization of catalysts

2.2.1. X-ray diffraction (XRD)

A Shimadzu 6000 diffractometer with a nickel filtered Cu K_α excitation source was employed to obtain XRD patterns of the catalyst samples. Compound identification was accomplished by the comparison of measured spectra of the samples with those of reference samples or JCPDS powder diffraction file data.

2.2.2. Infrared spectroscopy

The infrared spectra were recorded on a Mattson Infinity FT-IR spectrometer in the range of 1100–4000 cm^{-1} using CaF$_2$ windows. The self-supporting disks of the samples were prepared by grinding catalyst samples and pressing at 15,000 psig. IR examinations were carried out using a vacuum cell equipped with CaF$_2$ windows. The samples in the vacuum cell were outgassed at 10^{-5} Torr for 2 h at 200°C and cooled to room temperature before recording the IR spectrum.

Pyridine adsorption experiments were performed by admitting pyridine vapor to the vacuum cell at 50°C and evacuating the cell for 2 h at 150°C.

CF$_3$CH$_2$Cl adsorption experiments were carried out by flowing CF$_3$CH$_2$Cl into the IR vacuum cell for 0.5 h at 200°C and degassing the cell with N$_2$ for 0.5 h at 200°C.

2.2.3. Surface area

Surface areas of the catalysts were determined by the modified BET method from the adsorption isotherms of nitrogen at liquid nitrogen temperature with the help of the Area-meter II.

3. Results and discussion

Catalytic activities of CrF$_3$/MgF$_2$–AlF$_3$ in various compositions of Mg and Al were tested for the fluorination of CF$_3$CH$_2$Cl to CF$_3$CH$_2$F. Table 1 and Fig. 1 show the catalytic activities

Fig. 1. Activity of CrF$_3$/MgF$_2$–AlF$_3$ catalyst for the fluorination of CF$_3$CH$_2$Cl.

and surface areas of the Cr–Mg–Al fluoride catalysts having molar ratios of Al/Mg ranging from 0 to 4. The catalytic activity gradually decreased as the molar ratio of Al/Mg increased up to the value of Al/Mg = 1 and increased again thereafter showing a V-shaped curve. As shown in Fig. 2, XRD patterns indicates the formation of a new compound in the molar range of $0 < $ Al/Mg ≤ 1. The newly formed compound, identified as MgAlF$_5$ · 1.5H$_2$O by the comparison with the data in the JCPDS powder diffraction file, is likely to function as a catalyst poison. As the molar amount of AlF$_3$ exceeds that of MgF$_2$, MgAlF$_5$ · 1.5H$_2$O phase gradually disappears and another XRD detectable phase at $d = 6.03$, 3.61, 3.05 starts to emerge. From the XRD patterns, the new species was identified as β-AlF$_3$ [11]. It is quite interesting to notice the formation of β-AlF$_3$ in the mixed support catalyst because only γ-AlF$_3$ was obtained from the reaction of AlCl$_3$ · 6H$_2$O or the mixture of AlCl$_3$ · 6H$_2$O and Cr(OH)$_3$ · xH$_2$O with HF, and it remained unchanged even after the fluorination reaction. Therefore, it is believed that the presence of MgAlF$_5$ · 1.5H$_2$O or MgF$_2$ is playing a certain role in the

Table 1
Catalytic activity of CrF$_3$/MgF$_2$–AlF$_3$ catalyst for the fluorination of CF$_3$CH$_2$Cl measured at 340°C (HF/CF$_3$CH$_2$Cl = 8/1)

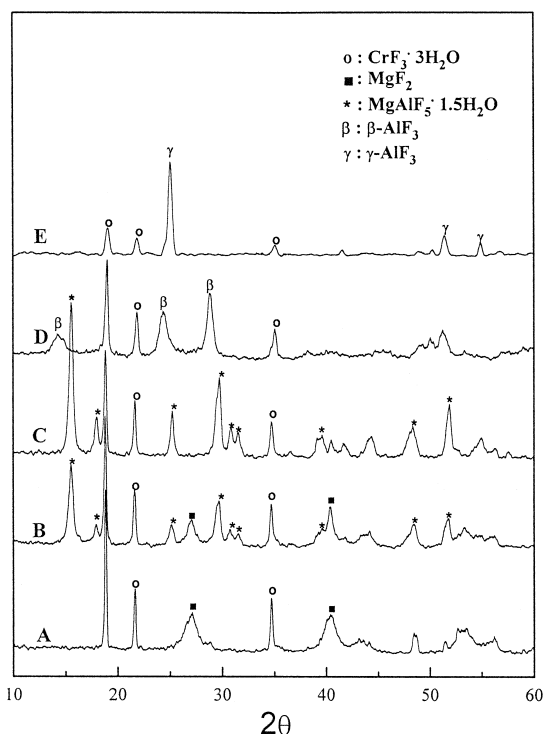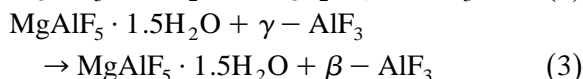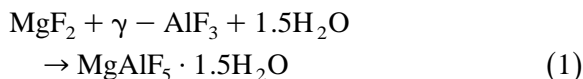| Entry	Molar ratio of CrF$_3$:MgF$_2$:AlF$_3$	Activity (mmol/h, g-cat)	Surface area (m^2/g)
A	1:4:0	0.59	61
B	1:3:1	0.25	47
C	1:2:2	0.14	41
D	1:1:3	0.48	69
E	1:0:4	0.55	73

Fig. 2. XRD Patterns of $CrF_3/MgF_2–AlF_3$ catalysts in various molar compositions of Cr/Mg/Al.

transformation of γ-AlF_3 into β-AlF_3 as in Eqs. (1)–(3).

$$MgF_2 + \gamma - AlF_3 + 1.5H_2O$$
$$\rightarrow MgAlF_5 \cdot 1.5H_2O \qquad (1)$$
$$MgAlF_5 \cdot 1.5H_2O \rightarrow MgF_2 + \beta - AlF_3 \qquad (2)$$
$$MgAlF_5 \cdot 1.5H_2O + \gamma - AlF_3$$
$$\rightarrow MgAlF_5 \cdot 1.5H_2O + \beta - AlF_3 \qquad (3)$$

Hess et al. [12], Kemnitz et al. [13] and Moerkerken et al. [14] reported that β-AlF_3 exhibits a higher catalytic activity and possesses stronger Lewis acidity compared with other aluminum fluoride species.

With this in mind, the catalytic activities of CrF_3/γ-AlF_3 and CrF_3/β-AlF_3 were compared in separate experiments performed at 340°C. As expected, CrF_3/β-AlF_3 showed a higher activity than CrF_3/γ-AlF_3 in the fluorination of CF_3CH_2Cl. It is, therefore, likely that the higher catalytic activity of CrF_3/MgF_2–AlF_3 (Mg/Al = 1/3) compared with CrF_3/MgF_2–AlF_3 (Mg/Al = 3/1) is attributed, in part, to the

presence of β-AlF_3 in spite of the fact that CrF_3/γ-AlF_3 is less active than CrF_3/MgF_2.

It has been proposed that fluorination and disproportionation catalysts must possess Lewis acidity to account for their activities [8]. In order to identify Brønsted acidity in the catalyst we performed pyridine adsorption experiments. Fig. 3 shows the IR spectra of adsorbed pyridine on the catalyst samples which were outgassed at 200°C after pyridine adsorption at 50°C. The spectrum obtained after pyridine adsorption was subtracted by the spectrum taken before pyridine adsorption for clarity. Adsorption bands were observed at 1450, 1490, 1545, 1577, and 1612 cm^{-1} on all of the samples. The bands at 1450 and 1612 cm^{-1} are commonly referred to pyridine coordinately bound to Lewis acid centers. The band at 1545 cm^{-1} is associated with the pyridinium ion resulting from the interaction of Brønsted acid sites with pyridine molecules. The intensities of the bands representing Lewis and Brønsted acidities increased with the increase of fluorination activity. Therefore, it can be concluded that the active sites of CrF_3/MgF_2–AlF_3 are closely related to both Lewis and Brønsted acidities.
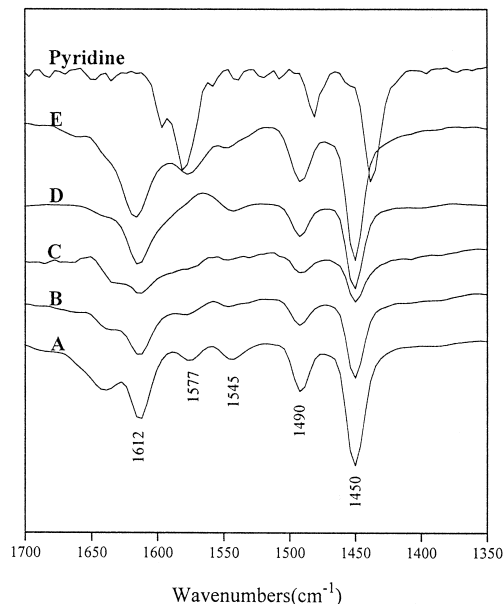

Fig. 3. IR spectra of adsorbed pyridine on CrF_3/MgF_2–AlF_3 catalysts in various molar compositions of Cr/Mg/Al.

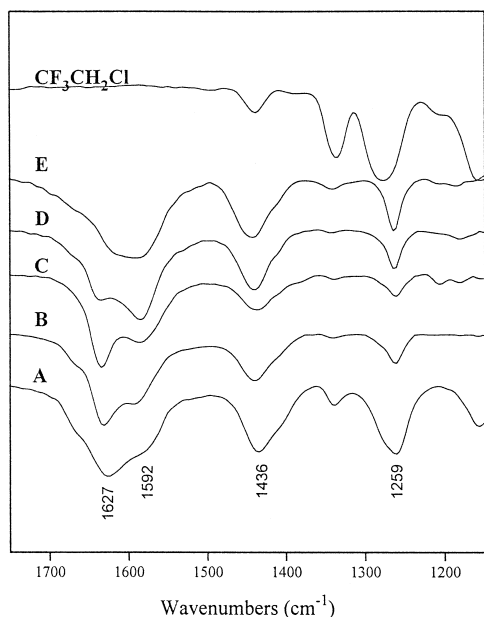Fig. 4. IR spectra of adsorbed CF_3CH_2Cl on CrF_3/MgF_2–AlF_3 in various molar compositions of Cr/Mg/Al.

Adsorption experiments were also performed with CF_3CH_2Cl in order to correlate the adsorption intensity with the fluorination activity. Fig. 4 shows the IR spectra of CF_3CH_2Cl adsorbed onto the CrF_3/MgF_2–AlF_3 catalyst samples. The intensities of adsorption bands were found much weaker for the most inactive catalyst sample, CrF_3/MgF_2–AlF_3 (Cr/Mg/Al = 1/2/2). This indicates that the formation of $MgAlF_5.1.5H_2O$ is inhibiting the adsorption of CF_3CH_2Cl and consequently lowering the fluorination activity.

4. Conclusion

The fluorination of CF_3CH_2Cl was performed over CrF_3 supported on MgF_2–AlF_3 (Al/Mg = 0–4) and the catalytic activities were compared with those of the single component support catalysts, CrF_3/MgF_2 or CrF_3/AlF_3, in order to see any synergy effect on the catalytic activity. Contrary to our expectation, the catalytic activities of mixed support catalysts, CrF_3/ MgF_2–AlF_3, were found to be considerably reduced compared with those of the single component support catalysts, CrF_3/MgF_2 and

CrF_3/AlF_3, indicating the presence of an anti-synergy effect between MgF_2 and AlF_3. XRD measurements show that such an antisynergy effect is mostly attributed to the formation of $MgAlF_5 \cdot 1.5H_2O$ which was found to reduce the fluorination activity. The observation of β-AlF_3 in the XRD patterns of the aluminum-rich catalysts (Al/Mg > 1) implies that $MgAlF_5 \cdot 1.5H_2O$ or MgF_2 is responsible for the transformation of γ-AlF_3 into β-AlF_3. FT-IR studies indicate that the fluorination activity is highly dependent on the strength of both Lewis and Brønsted acidities on the catalyst. FT-IR experiments show that the intensities of the adsorption bands of CF_3CH_2Cl adsorbed on the catalysts diminish as the catalytic activity decreases.

Acknowledgements

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