Catalytic fluorination of 1,1,1-trifluoro-2-chloroethane (HCFC-133a) over chromium catalysts

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Received 4 March 1998; accepted 3 June 1998

Catalytic fluorination of HCFC-133a was performed over various forms unsupported and supported chromium oxides. Catalytic activity is strongly dependent on the morphological structure of chromia. Increased conversion is observed as the crystallinity of chromia decreases. The best catalytic activity and strongest resistance against deactivation observed with CrOx/MgO is attributed to the presence of highly dispersed chromium species (isolated Cr(VI) and oligomeric Cr–O–Cr species) on the support surface.

Keywords: fluorination, HCFC-133a, chromia catalysts, support effect

1. Introduction

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 foam blowing application. Therefore, many routes for producing HFC-134a have been developed. One of popular methods is fluorination of HCFC-133a (1,1,1-trifluoro-2-chloroethane) using chromium oxide or supported metal catalysts [1–10]. Lu et al. have observed that the catalytic activity of CrF_3/α-AlF_3 is proportional to the surface area of the α-AlF_3 support or to that of CrF_3 [9]. Brunet et al. claimed that catalytic activity of fluorinated chromium oxide is proportional to the number of reversibly oxidized sites on the chromium oxide [10]. However, there has been no investigation on the surface structure and active sites of the chromium catalysts in relation to their catalytic activity.

In this paper, we have tested various unsupported and supported chromium catalysts for the gas-phase catalytic fluorination of HCFC-133a (1,1,1-trifluoro-2-chloroethane) with HF. Catalytic activity was correlated with structural properties of chromium species which was characterized by means of Raman and XRD.

2. Experimental

2.1. Preparation of catalysts

Unsupported chromia hydrogel was prepared by the precipitation method; an ammoniacal solution was added to a stirring solution of chromium nitrate at a constant rate. After completing precipitation at pH of 7.0, the hydroxide formed was aged for another 4 h. It was then filtered and washed several times with distilled water and, finally, dried in an oven at 135 °C for 12 h. The dried chromia hydrogel was subject to various pre-treatments to yield different structures of chromium oxides [11].

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

Sample B: heated in flowing helium at 400 °C for 4 h.

Sample C: heated in flowing helium at 800 °C for 4 h.

Sample D: commercial chromia (from Aldrich).

Supported chromium catalysts were also prepared by the same precipitating method as unsupported chromia, except that the chromium nitrate solution was replaced by a chromium nitrate solution containing the support slurry. The dried precipitates were subject to calcination at 450 °C for 4 h. The supports used for the loading of Cr were Al_2O_3 (Aldrich, 260 m^2/g), TiO_2 (JRC-TiO-3, 48.5 m^2/g), ZrO_2 (Aldrich, 50 m^2/g), MgO (Alfa, 10 m^2/g), AlF_3 and MgF_2. The MgF_2 support was prepared by fluorinating MgO powder with HF at room temperature. The fluorination reaction was carried out by introducing liquid HF drop by drop to an aqueous solution of suspended MgO that was kept at a constant stirring. After introducing 20% excess HF for converting MgO to MgF_2, the slurry was aged for 2 h to complete the reaction. Filtering and drying the precipitate yielded MgF_2 (64 m^2/g) supports. The AlF_3 support was prepared according to the method described previously [12]. Al_2O_3 (Aldrich, 260 m^2/g) is heated with an aqueous solution of NH_4F in a reaction vessel at 100 °C for 30 min, the precipitated slurry was calcined at 450 °C for 4 h.

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2.2. Reaction test

Fluorination of HCFC-133a was carried out at 370 °C under atmospheric pressure using a fixed-bed reactor, which was made of 3/8 inch inconel tubing. Hydrogen fluoride and HCFC-133a were diluted in helium to keep the mole ratio of HCFC-133a/HF/He at 1/8/5. Total flow rate was kept at 30 ml/min. In general, before carrying out the reaction, catalyst was activated by He at 400 °C for 4 h, then this was followed by fluorination with HF (16 ml/min) at 370 °C for 2 h. The gaseous products were analyzed by a gas chromatograph with a Porapak T column (80/100 mesh, 150 cm) and a thermal conductivity detector.

2.3. Characterization of catalysts

X-ray diffraction measurements were performed using a diffractometer (Rigaku DMAX-B) with Cu Kα radiation. The specific surface areas were determined by the BET method using a Micromeritics (Accusorb 2100E) apparatus. Raman specta were obtained with an Ar^+ laser (model 532-RENS-A01) delivering 1–100 mW incident radiation to the sample, where the exciting line was typically 514.5 nm. The scattered radiation was detected in Wright instruments with an intensified photodiode array cooled thermoelectrically to −30 °C. All Raman spectra were obtained at room temperature and under ambient condition.

3. Results and discussion

Results of the reaction test for unsupported chromium oxides are presented in table 1. The main reaction product is HFC-134a (CF_3CH_2F), which is formed by the halogen exchange reaction between HCFC-133a and HF. Also, a small amount of CF_2CHCl as a by-product is produced by dehydrofluorination of HCFC-133a even in the presence of HF. Both the conversion of HCFC-133a and the selectivity to HFC-134a increase in the order D < C < B < A, which is the same as the order of increasing surface area. Therefore, the catalytic activity (conversion) seems to be proportional to the surface area as claimed previously [9]. Figure 1 shows that the crystallinity of α-Cr_2O_3 also decreases in the order of D < C < B < A, indicating that crystallinity is another important factor for correlating with activity. With the surface area alone, it is not easy to explain the selectivity increase with increased surface area if the same crystallinity is assumed. Moreover, the zero conversion (catalytic inertness) that was observed with fully crystallized Cr_2O_3 (sample D) implies that crystallinity is more important factor than the surface area for correlating catalytic activity.

Dispersing chromia on support is another simple way to decrease particle size and crystallinity of chromia. Several supports were screened, and table 2 shows the results

Table 1
Catalytic activity for unsupported chromium oxides in the fluorination reaction.

Catalyst	Surface area[a] (m^2/g)	Conversion (%)	Selectivity (%)	
			HFC-134a	CF_2CHCl
A	162 (110)	24.4	97.5	0.7
B	80 (60)	15.8	96.8	1.4
C	20 (14)	6.1	93.1	5.1
D	7 (7)	0.0	0.0	0.0

[a] The value in parentheses represents the surface area measured after the fluorination reaction.

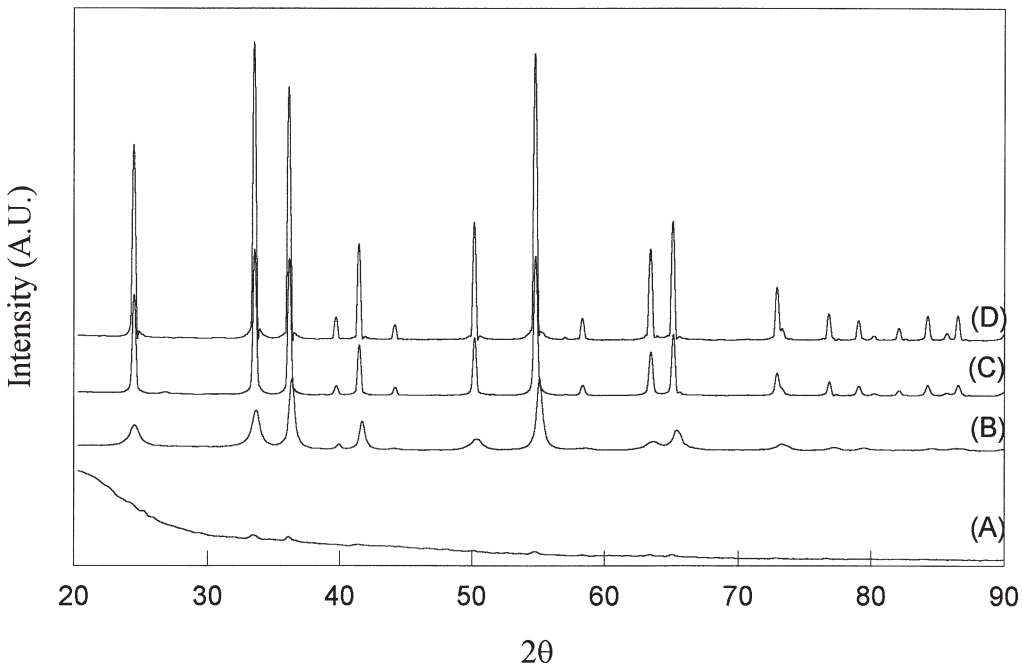

Figure 1. XRD patterns of pure chromium oxide. (A) Sample A, (B) sample B, (C) sample C, (D) sample D.

Table 2
Conversions of HCFC-133a and selectivities to HFC-134a for chromium oxide supported on various supports (GHSV = 1800 l/kg_{cat} h).

Catalyst	Surface area ($m^2\ g^{-1}$) after reaction	Temperature (°C)					
		320		350		370	
		Conv. (%)	Select. (%)	Conv. (%)	Select. (%)	Conv. (%)	Select. (%)
CrOx/MgO	80.0	9.8	98.4	21.4	98.9	25.9	98.8
$CrOx/Al_2O_3$	140.0	4.5	98.0	10.5	97.0	17.3	96.2
$CrOx/AlF_3$	28.5	2.1	86.8	5.3	93.4	14.2	95.3
$CrOx/MgF_2$	60.0	1.1	85.1	4.0	93.0	8.6	97.6
$CrOx/TiO_2$	48.3	–	–	–	–	12.0	94.2
$CrOx/ZrO_2$	48.0	0.0	0.0	0.0	0.0	0.0	0.0

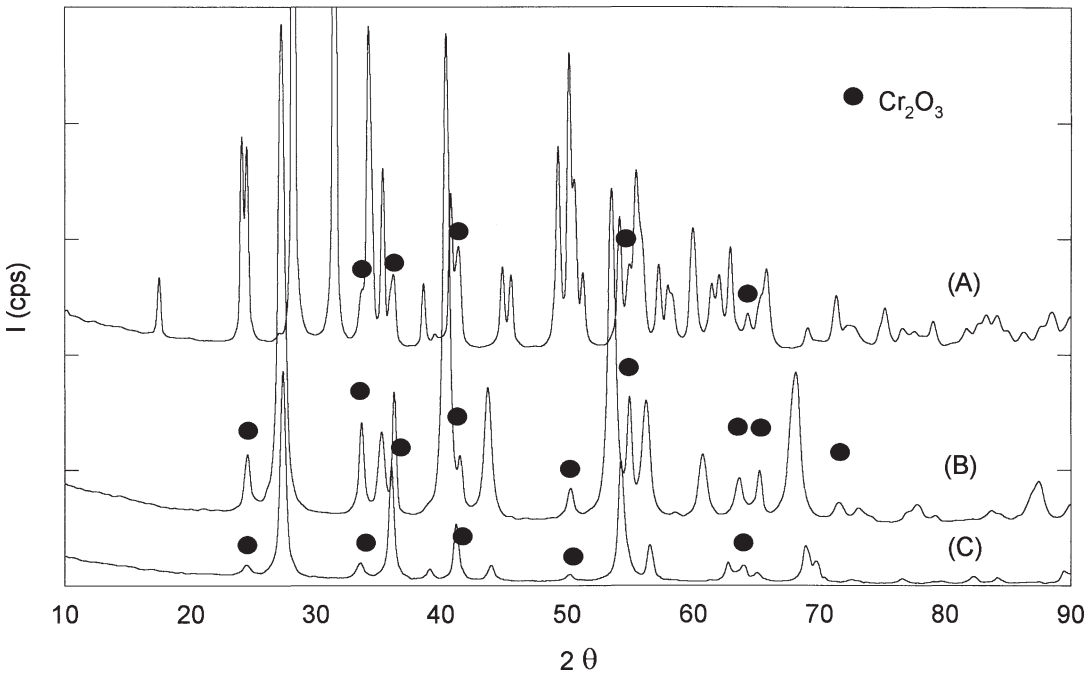

Figure 2. XRD patterns of chromium oxide supported on various supports (after the catalysts were activated with He at 400 °C). (A) $CrOx/ZrO_2$, (B) $CrOx/MgF_2$, (C) $CrOx/TiO_2$.

of reaction tests for representative supports. The conversion decreases in the order of MgO > Al_2O_3 > AlF_3 > MgF_2 > TiO_2. Almost zero conversion is observed for ZrO_2. The selectivity to HFC-134a is not strongly dependent on the support type, but highest with MgO. The catalytic activity obtained with Cr/MgO is the highest among various chromium catalysts that have been tested so far [1–4]. Figure 2 shows the results of X-ray diffraction analyses for the supported catalysts (taken before the prefluorination). A fully developed crystalline phase of Cr_2O_3 is observed for ZrO_2, TiO_2 and MgF_2. Chromia supported on MgO, Al_2O_3 or AlF_3 has been found to be X-ray amorphous, which suggests a high dispersion of the chromia particle.

For the Cr/MgO catalyst, the effect of chromium oxide loading on the conversion of HCFC-133a and the selectivity to HFC-134a are shown in figure 3. As the chromium oxide content increases, the conversion increases gradually showing a maximum point at 15% chromium content. The selectivity stays more or less constant after initial increases at low Cr contents. Figure 4 shows Raman spectra of the CrOx/MgO catalysts that were taken before the prefluorination. The catalysts having low Cr contents (5, 10 and 15 wt%) show two strong bands, whereas 20 wt% Cr/MgO catalyst shows splitting of the two bands. It is well known that tetrahedrally coordinated molecules of isolated monomeric CrO_4^{2-} in aqueous solution possess four Raman-active fundamental modes of vibration: symmetric and antisymmetric stretching modes at 846 and 904 cm^{-1} and two bending modes at 371 and 348 cm^{-1}. In the case of dimers, trimers and tetramers, bands assigned to CrO_2 chain appear at 956–987 cm^{-1}, and bands of Cr–O–Cr linkage at 772–884 cm^{-1}, 525–557 cm^{-1} and 209–217 cm^{-1} [13–15]. Thus, for the catalysts of 5, 10 and 15 wt% Cr/MgO, the bands at 880 and 840 cm^{-1} are assigned to stretching modes, and the single band at 375 cm^{-1} to the bending mode of an isolated (monomeric) chromate species. The appearance of an additional weak

Table 3
Deactivation tendency after pretreatment of HCFC-133a.

Catalyst	Surface area (m^2/g) after reaction	Conversion for fresh sample	Conversion after pretreatment of HCFC-133a	Degree of deactivation[a] (%)
A	110	23.8	21.9	92.0
B	60	15.3	6.3	41.2
C	14	6.1	1.0	16.4
Cr/MgO	80	25.6	25.0	97.6

[a] (Conversion of deactivated cat./conversion of fresh cat.) × 100.

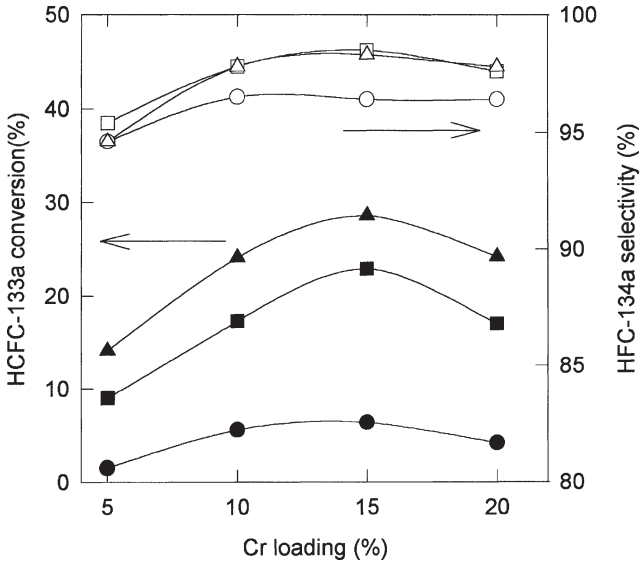

Figure 3. Effect of loading of Cr on the conversion of HCFC-133a and the selectivity to HFC-134a (HF/He/HCFC-133a = 8/5/1, GHSV = 1800 l/kg_{cat} h). (●, ○) 320 °C, (■, □) 350 °C, (▲, △) 370 °C.

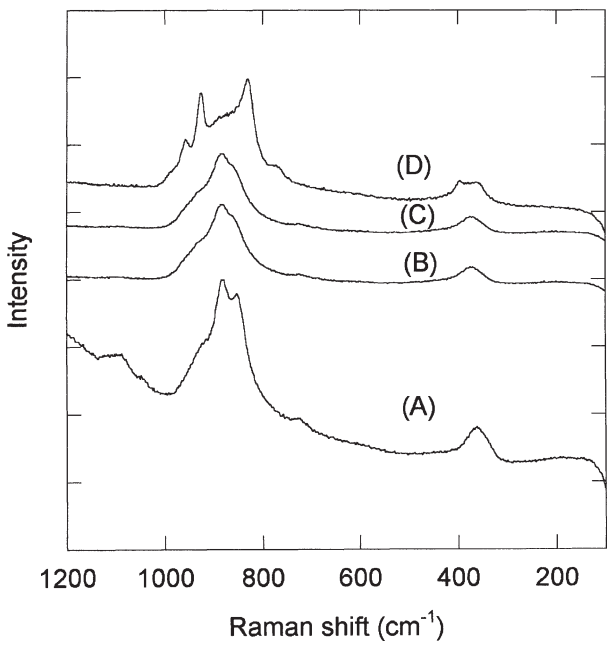

Figure 4. Raman spectra of CrOx/MgO as a function of loading of Cr (after the catalysts were activated with He at 400 °C). (A) 5 wt%, (B) 10 wt%, (C) 15 wt%, (D) 20 wt%.

shoulder band at 940 cm^{-1} indicates the presence of polymeric Cr–O species in a minor amount. For the 20 wt% Cr/MgO, the observation of new bands that appear at 820, 920 and 960 cm^{-1} confirms the presence of polymeric (dimer to tetramer) chromate species. Therefore, a decrease of conversion with 20 wt% Cr/MgO catalyst is attributed to the presence of polymeric chromium species. Brunet et al. [10] have suggested that the catalytic activity is proportional to the number of reversibly oxidized sites measured by temperature-programmed reduction with hydrogen. The results are in agreement with our observation, since oxygens in the monomeric chromium species must be more mobile that those in polymeric chromium species.

Fluorination reaction occurring on the surface of chromia is accompanied by dehydrofluorination of HCFC-133a, which is known to be responsible for the deactivation of chromia via coking of HCFC-133a [10]. To investigate the deactivation by HCFC-133a, several chromium catalysts that were prefluorinated at 370 °C for 2 h were pretreated with HCFC-133a for 9 h before carrying out the fluorination reaction. The pretreatment conditions are as follows: He/HCFC-133a = 5/1 and GHSV = 720 l/kg_{cat} h. As shown in table 3, the extent of deactivation is increased in the order of the sample A < B < C in the case of unsupported chromium catalysts. Increased crystallinity of chromium oxide accelerates the deactivation. Least deactivation can be found with the chromium oxide supported on MgO. The results suggest that isolated and/or oligomeric chromium species are responsible for the high catalytic activity and strong resistance against deactivation by HCFC-133a.

Acknowledgement

We thank Korea Science and Engineering Foundation through the Research Center for Catalytic Technology at POSTECH and the CFC alternatives research center of Korea Institute of Science and Technology for financial support of this work.

References

[1] S.L. Bell, US Patent 4 129 603 (1978).
[2] S.E. Potter, US Patent 4 153 675 (1979).

[3] J.D. Scott and M.J. Watson, US Patent 5 449 656 (1995).
[4] S. Brunet, B. Requieme, E. Colnay, J. Barrault and M. Blanchard, Appl. Catal. B 5 (1995) 305.
[5] J. Barrault, S. Brunet, B. Requieme and M. Blanchard, J. Chem. Soc. Chem. Commum. (1993) 374.
[6] H. Quan, Z. Li, H. Yang, J. Lu, J. Ren, S. Chen, H. Li and H. Li, Appl. Catal. B 8 (1996) 209.
[7] H. Kim, H.S. Kim, B.G. Lee, H. Lee and S. Kim, J. Chem. Soc. Chem. Commun. (1993) 374.
[8] H. Lee, H.D. Jeong, Y.S. Chung, H.K. Lee and M.J. Chung, J. Catal. 169 (1997) 307.
[9] J. Lu, H. Yang, S. Chen, L. Shi, J. Ren, H. Li and S. Peng, Catal. Lett. 41 (1996) 221.
[10] S. Brunet, B. Requieme, E. Matouba, J. Barrault and M. Blanchard, J. Catal. 152 (1995) 70.
[11] M.P. Mcdaniel and R.L. Burwell, Jr., J. Catal. 36 (1975) 394.
[12] H.J. Reitsma and C. Boelhouwer, J. Catal. 33 (1974) 39.
[13] G. Michel and R. Cahay, J. Raman Spectr. 17 (1986) 4.
[14] G. Michel and R. Machiroux, J. Raman Spectr. 14 (1983) 22.
[15] M.A. Vuurman, D.J. Stufkens, A. Oskam, J.A. Moulin and F. Kapteijn, J. Mol. Catal. 60 (1990) 83.