Effect of Magnesium Fluoride in Chromium–Magnesium Catalysts on the Fluorination Reaction of 1,1,1-Trifluoro-2-chloroethane

Honggon Kim,*[a] Hoon S. Kim,[a] Byung G. Lee,[a] Hyunjoo Lee[a] and Sehoon Kim[b]

[a] *CFC Center, Korea Institute of Science and Technology, Seoul 136-791, Korea*
[b] *Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea*

Magnesium fluoride, mixed with chromium fluoride, enhances the activity, selectivity and lifetime of the chromium catalyst for the vapour-phase fluorination of CF_3CH_2Cl with anhydrous HF to give CF_3CH_2F.

CF_3CH_2F (HFC-134a) is considered as one of the most promising candidates for the substitution of CFC-12 (CF_2Cl_2).[1,2] One of the synthetic routes to HFC-134a is the vapour-phase fluorination of CF_3CH_2Cl (HCFC-133a) with HF over Cr- or Al-based catalysts. Among various fluorination catalysts, the characteristics of Cr_2O_3 have been extensively examined.[3–6] However, Cr_2O_3 has been found rapidly deactivated during the fluorination of HCFC-133a, which is a major drawback in its industrial application.

We initially assumed that only a small portion of the surface chromia was fluorinated, which could be the reason for the fast deactivation of Cr_2O_3. $CrF_3{\cdot}4H_2O$ was chosen as the catalyst precursor on the assumption that high fluorine-containing catalysts might have better catalytic activity and a longer lifetime. Cylindrical extrudates of $CrF_3{\cdot}4H_2O$ (30 g) were loaded in an Inconel 600 reactor, dried *in situ* at 400 °C for 1 h under He, then activated with HF at 200 °C for 2 h, and at 400 °C for 1 h. The fluorination reaction was conducted at 360 °C at atmospheric pressure. Contrary to our expectation, the fluorination of HCFC-133a with HF over $CrF_3{\cdot}4H_2O$ gave only a small amount of the desired product, HFC-134a, in 1.5% yield and an appreciable amount of an unwanted product, $CF_2{=}CHCl$, (HCFC-1122) in 1.1% yield.

Since $CrF_3{\cdot}4H_2O$ had a small specific surface area (8 $m^2\,g^{-1}$), we mixed MgF_2, which is inactive for the fluorination of HCFC-133a, with $CrF_3{\cdot}4H_2O$ to increase the surface area of the catalyst. Surprisingly, the catalytic activity increased significantly, by more than 11 times the amount when $CrF_3{\cdot}4H_2O$ was used alone, even though the surface area of the catalyst increased by only four times (Table 1). Furthermore, the formation of HCFC-1122, which is known to be responsible for the deactivation of Cr catalysts, was significantly reduced, to less than 0.05%. Variation in molar composition of the mixed catalyst, ranging from $CrF_3{\cdot}4H_2O:MgF_2$ = 0.1 to 10, showed only a slight difference in the fluorination activities. In addition, unlike Cr_2O_3, the catalytic activities of the mixtures remained almost unchanged with the reaction time up to 200 h at 360 °C.

As shown in Fig. 1, the XRD pattern of the mixture of $CrF_3{\cdot}4H_2O$ and MgF_2 is different from that of $CrF_3{\cdot}4H_2O$, indicating the formation of new chromium species. In addition, the crystallinity of MgF_2 is markedly reduced when mixed with $CrF_3{\cdot}4H_2O$. This suggests that a large portion of MgF_2 exists in an amorphous state when in the mixture. The newly formed chromium species is presumed to be $CrF_3{\cdot}3H_2O$ by comparing its XRD pattern with the XRD pattern of authentic $CrF_3{\cdot}3H_2O$ as well as with the standard XRD pattern in the library. Without the addition of MgF_2, the new chromium species was not obtained by the thermal treatment of $CrF_3{\cdot}4H_2O$ in N_2 or in air up to 360 °C. Another new possible species proposed is a Mg–Cr salt such as $MgCrO_xF_y$[7] which potentially forms in the mixture of $CrF_3{\cdot}4H_2O$ and MgF_2. These new Cr-containing species could be the active centre for the fluorination reaction.

Solid-state ^{19}F NMR spectroscopy was applied to $CrF_3{\cdot}4H_2O$, and to the mixture of $CrF_3{\cdot}4H_2O$ and MgF_2 to help identify the new chromium species in the mixture. However, the spectra of the solids did not show any difference in the samples, due to the very poor spectral resolution. As both $CrF_3{\cdot}4H_2O$ and the mixture of $CrF_3{\cdot}4H_2O$ and MgF_2 were slightly soluble in water, ^{19}F NMR spectra were taken in D_2O with CF_3CO_2D as an internal standard. The spectrum of $CrF_3{\cdot}4H_2O$ shows four peaks at δ −51.761, −67.458, −73.040 and −88.278, while the mixture gives only three peaks at δ −50.625, −65.539 and

Table 1 Product distribution of HCFC-133a fluorination

Molar ratio of CrF_3:MgF_2	Surface area of catalyst/$m^2\,g^{-1}$ [a]	Product distribution (mol%) HFC-134a	HCFC-1122
CrF_3 alone	8	1.5	1.1
10:1	31	16.9	0.6
5:1	47	17.8	0.3
1:1	79	20.7	0.0
0.5:1	84	21.1	0.0
0.25:1	93	20.7	0.0
0.1:1	94	19.4	0.0
MgF_2 alone	102	0.7	0.2

[a] Specific surface area of the catalysts measured before the fluorination reaction

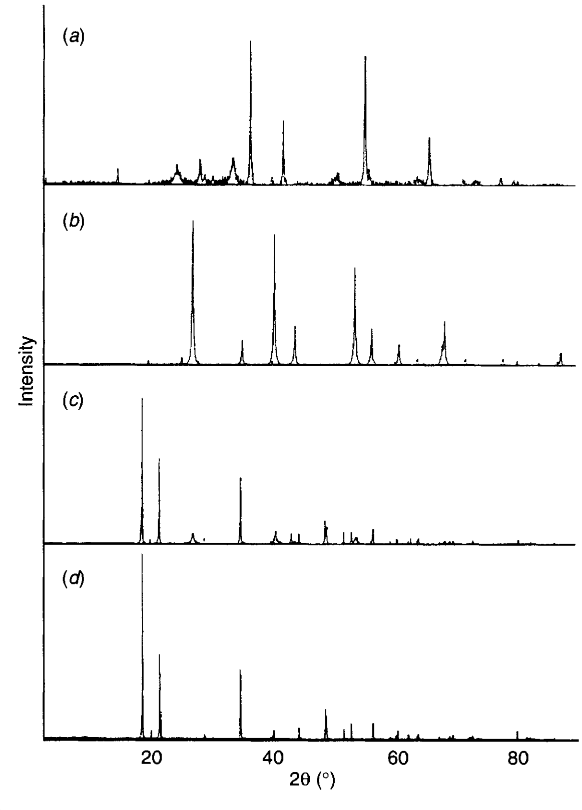

Fig. 1 XRD Powder patterns of (*a*) $CrF_3{\cdot}4H_2O$ (×5), (*b*) MgF_2 (×1), (*c*) the mixture of $CrF_3{\cdot}4H_2O$ and MgF_2 (molar ratio of Cr:Mg = 1:2, ×1), (*d*) $CrF_3{\cdot}3H_2O$ (×3)

−72.806. This result again indicates that the chromium species in the mixture is different from $CrF_3 \cdot 4H_2O$.

Brunet[5] and Coulson[8] reported that the catalytic activity of Cr_2O_3 is proportional to the number of chromium atoms having an oxidation state higher than three. Measurement of the high-valent (> + 3) chromium by titration technique showed that both $CrF_3 \cdot 4H_2O$ and the mixture of CrF_3–MgF_2 have negligible oxidizing capacities, *ca.* 5.5 x 10^{-5} F g^{-1} of catalyst. This result could indicate that the active sites of CrF_3–MgF_2 for fluorination are not closely related to the amount of the high-valent chromium species existing on the catalyst's surface.

From the above results it is deduced that besides increasing the catalyst's surface area, MgF_2 plays an important role in lengthening the lifetime of the chromium catalyst by suppressing the formation of CF_2=CHCl. In addition, MgF_2 enhances the fluorination activity, possibly through an electronic interaction with CrF_3 or by forming a new metal salt such as $MgCrO_xF_y$.

Electronic spectroscopy in chemical analyses studies are under way to elucidate the role of MgF_2 and to characterize the active chromium species. Fluorination activities are also under examination with various forms of $MgCrO_xF_y$ which might be prepared from various CrO_xF_y and MgF_2.

Received, 17th July 1995; Com. 5/04658K

References

1 G. Webb and J. Winfield, *Chem. Br.*, 1992, 996.
2 T. P. Nelson and S. L. Wevill, *Alternative Formulations and Packaging to Reduced Use of Chlorofluorocarbons*, Noyes Data Co., New Jersey, 1990.
3 W. H. Gumprecht, L. E. Manzer and V. N. Mallikarjuna Rao, *US Pat.*, 4 843 181, 1989.
4 J. Barrault, S. Brunet, B. Requieme and M. Blanchard, *J. Chem. Soc., Chem. Commun.*, 1993, 374.
5 S. Brunet, B. Requieme, E. Matouba, J. Barrault and M. Blanchard, *J. Catal.*, 1995, **152**, 70.
6 L. Marangoni, G. Rasia, C. Gervasutti and L. Columbo, *La Chim. Ind.*, 1982, **64**, 135.
7 S. D. Brown, P. J. Green and G. L. Gard, *J. Fluorine Chem.*, 1975, **5**, 203.
8 D. R. Coulson, P. W. J. G. Wijnen, J. J. Lerou and L. E. Manger, *J. Catal.*, 1993, **140**, 103.