

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

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Magnesium fluoride, mixed with chromium fluoride, enhances the activity, selectivity and lifetime of the chromium catalyst for the vapour-phase fluorination of CF₃CH₂Cl with anhydrous HF to give CF₃CH₂F.

CF₃CH₂F (HFC-134a) is considered as one of the most promising candidates for the substitution of CFC-12 (CF₂Cl₂).^{1,2} One of the synthetic routes to HFC-134a is the vapour-phase fluorination of CF₃CH₂Cl (HCFC-133a) with HF over Cr- or Al-based catalysts. Among various fluorination catalysts, the characteristics of Cr₂O₃ have been extensively examined.^{3–6} However, Cr₂O₃ 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 Cr₂O₃. CrF₃·4H₂O 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 CrF₃·4H₂O (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 CrF₃·4H₂O gave only a small amount of the desired product, HFC-134a, in 1.5% yield and an appreciable amount of an unwanted product, CF₂=CHCl, (HCFC-1122) in 1.1% yield.

Since CrF₃·4H₂O had a small specific surface area (8 m² g^{–1}), we mixed MgF₂, which is inactive for the fluorination of HCFC-133a, with CrF₃·4H₂O to increase the surface area of the catalyst. Surprisingly, the catalytic activity increased significantly, by more than 11 times the amount when CrF₃·4H₂O 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 CrF₃·4H₂O:MgF₂ = 0.1 to 10, showed only a slight difference in the fluorination activities. In addition, unlike Cr₂O₃, 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 CrF₃·4H₂O and MgF₂ is different from that of CrF₃·4H₂O, indicating the formation of new chromium species. In addition,

the crystallinity of MgF₂ is markedly reduced when mixed with CrF₃·4H₂O. This suggests that a large portion of MgF₂ exists in an amorphous state when in the mixture. The newly formed chromium species is presumed to be CrF₃·3H₂O by comparing its XRD pattern with the XRD pattern of authentic CrF₃·3H₂O as well as with the standard XRD pattern in the library. Without the addition of MgF₂, the new chromium species was not obtained by the thermal treatment of CrF₃·4H₂O in N₂ 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 CrF₃·4H₂O and MgF₂. These new Cr-containing species could be the active centre for the fluorination reaction.

Solid-state ¹⁹F NMR spectroscopy was applied to CrF₃·4H₂O, and to the mixture of CrF₃·4H₂O and MgF₂ 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 CrF₃·4H₂O and the mixture of CrF₃·4H₂O and MgF₂ were slightly soluble in water, ¹⁹F NMR spectra were taken in D₂O with CF₃CO₂D as an internal standard. The spectrum of CrF₃·4H₂O 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

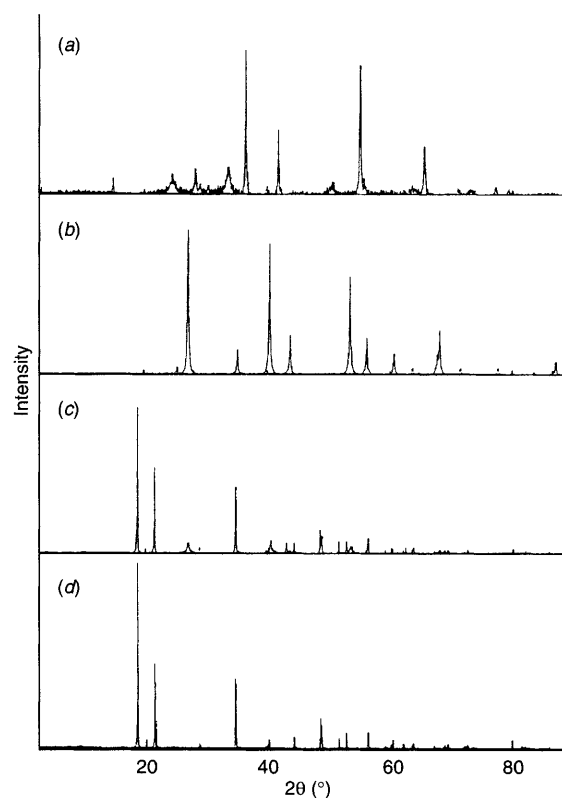


Fig. 1 XRD Powder patterns of (a) CrF₃·4H₂O (×5), (b) MgF₂ (×1), (c) the mixture of CrF₃·4H₂O and MgF₂ (molar ratio of Cr:Mg = 1:2, ×1), (d) CrF₃·3H₂O (×3)

–72.806. This result again indicates that the chromium species in the mixture is different from $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$.

Brunet⁵ and Coulson⁸ 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 $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ and the mixture of CrF_3 – MgF_2 have negligible oxidizing capacities, ca. $5.5 \times 10^{-5} \text{ F g}^{-1}$ 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 $\text{CF}_2=\text{CHCl}$. 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

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