Hydrodechlorination of CCl_2FCClF_2 over $NiO-Cr_2O_3$ catalysts

Susumu Okazaki* and Hisashi Habutsu

Department of Industrial Chemistry, Faculty of Engineering, Ibaraki University, Nakanarusawa, Hitachi-shi 316 (Japan)

Abstract

The vapor-phase hydrodechlorination of CCl_2FCClF_2

$$CCl_2FCClF_2 + H_2 \longrightarrow ClFC{=}CF_2 + HFC{=}CF_2 + HCl$$

is promoted at around 400 °C by $NiO-Cr_2O_3$, especially by a mixture containing 70 at% of Cr. The catalytic activity of the mixed oxide is well maintained, and nearly 100% conversion was observed even after a running time of 5 25 h. However, the reaction was not promoted by Cr_2O_3 alone, and CH_4 formation and deactivation due to carbonaceous deposit on the surface were markedly promoted by NiO and NiO–Cr_2O_3 containing smaller amounts of Cr_2O_3. By reference to the results of XRD and XPS measurements, the excellent catalytic behavior of $NiO-Cr_2O_3$ (Cr content: 70 at%) was attributed to $NiCr_2O_4$ being dispersed by Cr_2O_3 on the surface

Introduction

The hydrodechlorination of CCl_2FCClF_2 (abbreviated as CFC-113) is potentially important for the disposal of chlorofluorocarbons which may destroy the ozone layer, and for the preparation of useful fluoro-olefins such as $ClFC{=}CF_2$ (CTFE) and $HFC{=}CF_2$ (TFE). Hydrodechlorination is known to be promoted by noble metals supported on active carbon [1], but the activity rapidly decreases with process time. The catalytic behavior of noble metals must be modified before their use as industrial catalysts. In recent years it was found that the catalytic activity of Pd was greatly improved by mixing with Bi or Tl [2]. Besides noble metals, less expensive metals or their oxides, such as NiO, were reported to be able to promote hydrodechlorination [1, 3, 4]. However, unlike the noble metals, NiO exhibited its catalytic activity only at fairly high temperatures, where it tended to promote a simple hydrogenation and C–C bond cleavage, resulting in poorly selective formation of CTFE and TFE. The problem has been solved by supporting the NiO on a suitable carrier [3]. In this study, we have attempted to improve the catalytic behavior of NiO by mixing it with other metal oxides.

---

*Author to whom correspondence should be addressed

Experimental

Reactants and catalysts

CTFE and TFE, both having a purity of higher than 99 5%, were supplied by the Mitsui–DuPont Fluorochemical Co. NiO and its mixed oxides were prepared by coprecipitation from their respective metal nitrate solutions with aqueous NH_3, followed by repeated washing with water to a pH of 7 or 9, then drying in air at 120 °C for 5 h. In addition, $NiO–SiO_2$, which is known to be the most popular supported Ni catalyst, was prepared using an alkyl silicate by adding aqueous KOH solution to the mixed solution of ethyl silicate and nickel nitrate, followed by washing and drying in a similar manner as above. For these oxides, $NiO–MO_x$, the content of M, expressed as at% [or (number of M atoms/total number of metal $(M + Ni)$ atoms) $\times$ 100] was kept in the range 30 to 90%, usually 70 at%, unless otherwise noted. The mixed ratio described above was determined by the ratio of Ni to M in solution. Preliminary experiments revealed that the surface composition, determined by ESCA, was reproducible, as long as the sample used in the study was carefully prepared by coprecipitation from the mixed solution of a constant Ni to M ratio. All the catalysts were heat-treated at 600 °C for 3 h in air immediately before use The catalysts were reduced in the reactor by a flow of H_2 at the reaction temperature before the start of the reaction.

Reaction procedures

The reactions were carried out using a conventional flow reactor packed with a catalyst fabricated into granules of 14–20 mesh size. Unless otherwise noted, the reactions were carried out at 400 °C, and continued for 3 or 5 h in order to determine the maintenance of activity of the catalyst.

Analysis of products was carried out by gas chromatography using a 3-m column packed with Porapak R, while raising the column temperature from 70 to 200 °C at a rate of 8 °C per minute.

Crystal structure and composition of the surface layer

XRD and XPS analyses were carried out to examine the textures and surface compositions of the oxide catalysts, by using a Geigerflex diffractometer (Rigaku Denki Co.) and an ESCA 750 (Shimazu Co.) instrument, respectively. For the XPS measurements, Mg $K\alpha$ radiation was employed, and the ratios of various elements were calculated from the areas of the spectral peaks on the basis of the photo-ionization cross section at 1245 eV, in units of the C_{1s} cross-sectional area [5]

Results and discussion

Catalytic activities of mixed oxides containing NiO and/or Cr_2O_3

As shown in Table 1, CFC-113 was converted almost completely over NiO and mixed oxides, and considerable amounts of CH_4 and $C_2Cl_2F_2$

TABLE 1

Catalytic activities of various NiO–Mo$_x$[a] catalysts

Catalyst	Conversion (mol %)	Selectivity (mol%)			
		CTFE	TFE	CH$_4$	C$_2$Cl$_2$F$_2$
NiO–Cr$_2$O$_3$	99.9	67.0	7.7	12.5	5.8
NiO–SiO$_2$	99.7	34.5	22.3	32.1	0.2
NiO–Al$_2$O$_3$	99.7	64.4	8.2	16.3	4.6
NiO–CuO	88.9	39.2	16.0	0.8	0.1

[a]Atomic ratio (Ni/M) = 1; process time, 15 min; reaction temperature, 400 °C; molecular ratio of reactants (H$_2$/CFC-113) = 3.7; flow rate of H$_2$, 50 ml/min (at STP).

TABLE 2

Catalytic activities of various MO$_x$–Cr$_2$O$_c$ catalysts[a]

Catalyst	Conversion (mol%)	Selectivity (mol%)			
		CTFE	TFE	CH$_4$	C$_2$Cl$_2$F$_2$
NiO–Cr$_2$O$_3$	99.7	58.9	11.7	4.9	6.7
CuO–Cr$_2$O$_3$	87.8	79.5	14.8	trace	1.4
Co$_2$O$_3$–Cr$_2$O$_3$	60.9	89.4	3.0	0.1	5.1
Fe$_2$O$_3$–Cr$_2$O$_3$	29.6	97.1	1.3	0	0.7
ZnO–Cr$_2$O$_3$	2.0	83.5	16.5	0	0

[a]Atomic ratio (M/Cr) = 1. These mixed oxides were prepared as for NiO–Cr$_2$O$_3$, although the final washing with water was at pH 7. Process time and reaction conditions were the same as those listed in Table 1.

were formed rather than the desired products CTFE and TFE. In particular, significant amounts of CH$_4$ were formed in the reaction catalyzed by NiO–SiO$_2$, similarly to that over NiO alone [1]. In terms of obtaining both high conversion and high CTFE selectivity, NiO–Cr$_2$O$_3$ was the best among the catalysts tested here. This result suggested that Cr$_2$O$_3$ might be especially suitable and effective as a component of the hydrodechlorination catalyst, and that other mixed oxides containing Cr$_2$O$_3$ might exhibit high catalytic activity for the reaction. Therefore the catalytic activities of some mixed oxides containing Cr$_2$O$_3$ were examined. As shown in Table 2, no other mixed oxide of chromium examined showed activity higher than that of NiO–Cr$_2$O$_3$.

Effect of the ratio of Ni to Cr on catalytic activity

The catalytic activity of NiO–Cr$_2$O$_3$ has been examined for samples composed of equal amounts of Ni and Cr. The catalytic activities of mixed oxides are, in general, highly dependent on the ratio of the constituents,
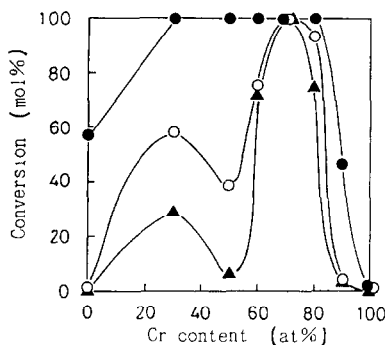
Fig 1   Effect of Cr content (Reaction conditions were the same as those shown in Table 1)
Process time (h)   ●, 1 25 h, ○, 3 25 h, ▲, 5 25 h

hence the effect of the ratio of NiO and Cr_2O_3 was examined, and the
results shown in Fig. 1 were obtained. As shown, NiO, which had consid-
erable catalytic activity at the beginning of the run, had a sharp loss of
activity with a longer process time. The catalytic performance was im-
proved by the addition of Cr_2O_3, although Cr_2O_3 itself was quite inactive
as a catalyst. The catalytic activity showed a maximum enhancement for
a Cr content of 70 at%. At the same time, the maintenance of catalytic
activity was improved by an increase in the Cr content to 70 at%.

The improvement in catalytic behavior described above shows that
Cr_2O_3 is a good promoter of NiO for catalytic hydrodechlorination How-
ever, two questions remained to be answered: Why was Cr_2O_3 especially
good as an additive to NiO? Why did the Cr_2O_3 content of 70 at% give the
biggest improvement? Before answering these problems, however, the
effect of the reaction temperature was examined, as catalytic behavior is,
in general, greatly affected by temperature.

Effect of reaction temperature

To understand the effect of temperature on the reaction over the
$NiO-Cr_2O_3$ catalyst, the reaction was also carried out at 350 and 450 °C.
The results (Table 3) indicate that the reaction was also nearly complete
at the lower temperature, and that the CTFE selectivity was somewhat
enhanced, possibly due to depression of TFE and CH_4 formation. How-
ever, at the lower temperature, the conversion rapidly decreased with
running time, as shown in Fig. 2. The reason for the rapid decrease is
unclear. However, the fact that a fair amount of $C_2Cl_2F_2$ was found in the
product suggested the occurrence of surface fluorination by HF formed by
a side reaction. $C_2Cl_2F_2$ may be formed by dehydrofluorination of
$CHClFCClF_2$ and/or $Cl_2FC-CHF_2$, which are possible intermediates in
the hydrodechlorination of CFC-113, and the resultant HF should convert
the surface metal oxides to their fluorides, which are inert as catalysts for
activation of H_2. On the other hand, in the reaction at 450 °C a high

TABLE 3

Effect of reaction temperature on the NiO CrO$_3$ catalyst[a]

Reaction temp (C)	Conversion (mol%)	Selectivity (mol%)			
		CTFE	TFE	CH$_4$	C$_2$Cl$_2$F$_2$
350	99 8	78 2	4 1	0 2	12 8
400	100 0	62 9	24 0	1 9	4 0
450	100 0	52 1	27 0	9 8	2 9

[a]Cr content of the NiO- Cr$_2$O$_3$ catalyst used was 70 at% Reaction conditions, other than the reaction temperature, were the same as those shown in Table 1
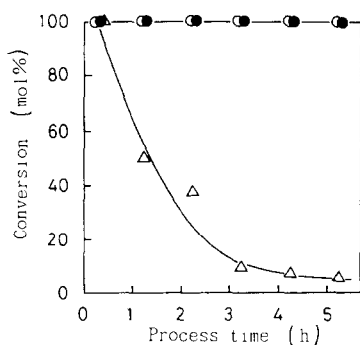
Fig 2 Effect of reaction temperature on maintenance of catalytic activity Reaction temperature △. 350 C, ○, 400 C, ●, 450 °C (Other reaction conditions and the catalyst were as described in Table 3.)

conversion, nearly 100%, was maintained during the 5 h run. However, the unwanted by-product CH$_4$, which may be formed through excessive hydrogenation and C–C bond cleavage, was produced in large amounts at the higher temperature. Thus, the high hydrogenation activity due to NiO might be suppressed by combination with Cr$_2$O$_3$ when the reaction temperature is raised to 450 °C

The results at the different temperatures show that a temperature of about 400 °C is best to obtain high CTFE and TFE selectivity and the maintenance of high activity for the reaction over a NiO–Cr$_2$O$_3$ catalyst.

Surface composition of the NiO–Cr$_2$O$_3$ catalysts

As shown in Fig. 1, the catalytic activity of NiO–Cr$_2$O$_3$ was a maximum when the Cr content was increased to 70 at%. However, the surface composition is generally different from that calculated from the mixing ratio of the raw materials. Therefore, the actual surface composition was examined by XPS. As Fig. 3 depicts, the surface Cr content was
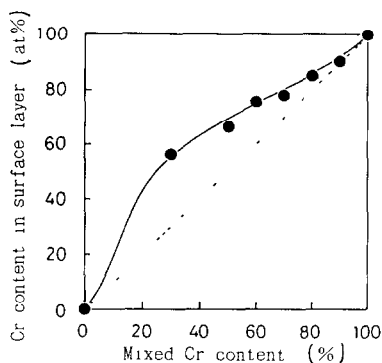
Fig 3 Relationship between the mixing ratio and the ratio detected in the surface layer after heat-treatment at 600 °C for 3 h followed by hydrogenation

found to be somewhat higher than that in the bulk, and the Cr content in the surface layer of the most active mixed oxide (Cr content: 70 at%) was found to be about 80 at%.

Crystal structures

As noted in the experimental section, the mixed oxide was heat-treated at 600 °C for 3 h in air, followed by H_2 treatment at the reaction temperature (usually 400 °C) for 1 h, immediately before use as a catalyst. The crystal structure, together with the chemical constitution at the surface should be modified by these treatments and by the mixing ratio of the raw materials. Furthermore, they were also modified by contact with the reactant CFC during use as a catalyst. The structure and consitution of the catalysts used were therefore examined by XRD analysis It was found, as shown in Fig. 4, that the reduction of NiO to Ni, which readily takes place for NiO alone, was suppressed on combination with Cr_2O_3, especially in large amounts. It was also found that $NiCr_2O_4$ was formed during the H_2 treatment and during use as a catalyst at a high temperature, although the mechanism of formation is not clear. The formation of $NiCr_2O_4$ became more marked when the amount of Cr_2O_3 was increased. Thus, it is probable that in the most active catalyst oxide (Cr content: 70 at%), most of the Ni in the surface layer is present in this form. Other than the peak due to this compound, peaks assignable to Cr_2O_3 were found in the XRD pattern of catalytically active $NiO-Cr_2O_3$ Since the atomic content of Cr in the surface layer was about 80 at%, or about four time that of the Ni, the catalytic activity may be assignable to $NiCr_2O_4$ dispersed on about the same amount of Cr_2O_3.

The oxidation state of the Ni component after H_2 treatment and after use as a catalyst was further examined by XPS. As shown in Fig. 5, a sharp peak due to Ni(0) was found in the spectrum of $Ni(2p_{2/3})$ for the NiO treated with H_2 at 600 °C This peak was observable, together with
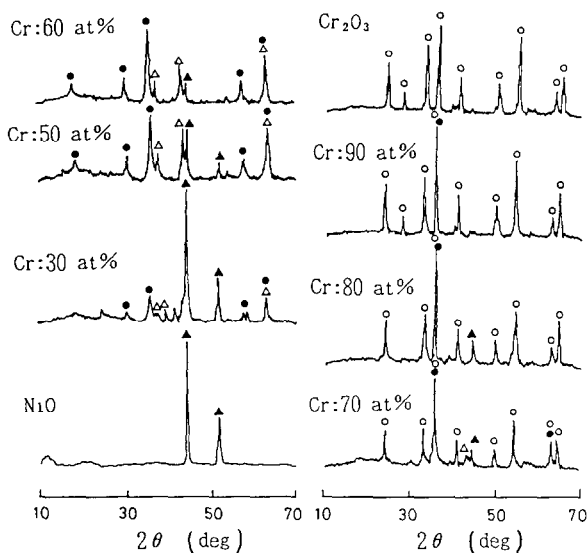
Fig 4 Crystal structures of NiO and various NiO Cr$_2$O$_3$ mixed oxides after use as catalysts at 400 °C for 5 25 h. ▲, Ni, △, NiO, ○, Cr$_2$O$_3$, ●, NiCr$_2$O$_4$ (Assignments of these peaks were carried out according to data from ref 7)

another at about 858 eV, in the spectrum of the mixed oxide. Nevertheless, the presence of Ni(0) was not ascertained by XRD. However, the peak from Ni(0) became fainter with increasing Cr content and, finally, there was only the peak ascribable to Ni^{2+} in the spectrum of the active mixed oxide (Cr content: 70 at%). These facts again suggest that the reduction of Ni^{2+} is suppressed by the presence of large amounts of Cr^{3-}, possibly because of formation of NiCr$_2$O$_4$.
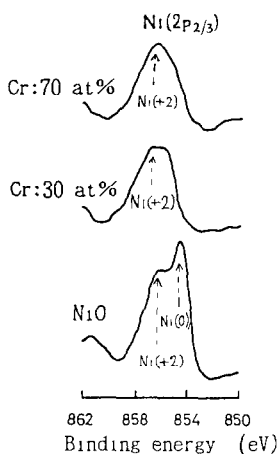

Fig 5 Peak position of Ni(2p) in NiO–Cr$_2$O$_3$ after heat-treatment at 600 °C for 3 h followed by hydrogenation

The presence of Cl and F components on the surface

Thermodynamically, Cr_2O_3 and NiO might be converted to their respective metal fluorides by reaction with HF. In addition, CFC-113 and intermediates formed from CFC-113 might directly react with the metal oxides as fluorinating agents. Similarly, surface chlorination also might occur during the catalytic hydrodechlorination. Hence, the amounts and the state of these halogens on the surface were examined by XPS. As shown in Table 4, there were amounts of F and Cl greater than 10% for samples containing small amounts of Cr.

The F(1s) signal was found at about 685 and 688 eV (Fig. 6) for samples containing small amounts of Cr (Cr contents· 30 and 50 at%). These peaks were assignable to metal–F (Cr–F or Ni-F) and C–F bonds, respectively. The latter, or the peak assignable to organic fluoride, decreased on increasing the proportion of Cr and, finally, was almost absent
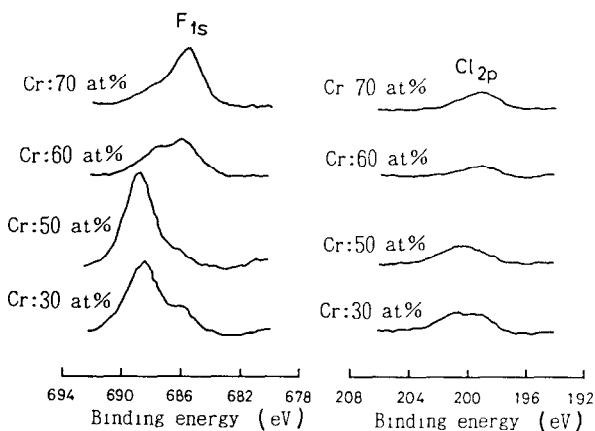

Fig 6 Peak positions of F(1s) and Cl(2p) in NiO -Cr$_2$O$_3$ after use as a catalyst at 400˚ C for 5 25 h

TABLE 4

F and Cl contents in the surface layer of the NiO Cr$_2$O$_3$

Cr content (at%)	Composition (%)			
	After 75 min		After 315 min	
	F	Cl	F	Cl
30	8 0	4 9	12 7	4 1
50	10 1	4 3	10 0	4 4
60	6 2	3 9	5 2	2 3
70	6 7	3 9	6 4	3 6

in the spectrum of the catalytically active mixed oxide (Cr content: 70 at%) A similar shift was also observed for the Cl(2p) peak with an increase in the Cr content. These facts suggested that the rapid decrease of catalytic activity with running time, which was especially marked for the mixed oxide containing a smaller amount of Cr (such as that shown in Fig. 1) was ascribable to accumulation of a carbonaceous deposit.

Reactivation of the $NiO-Cr_2O_3$ catalyst

If the decrease in catalytic activity is due to the accumulation described above, the deactivated catalyst could be regenerated merely by air oxidation. Confirmation of the effectiveness of the oxidation is also important from the viewpoint of practical use of the mixed oxide as a catalyst. In this test, mixed oxide containing 1.1 atomic amounts of Cr and Ni was used because it does not maintain catalytic activity as well as the mixed oxide containing 70 at%, as shown in Fig. 1. As a result of this test (see Fig. 7), air oxidation was found to be fairly effective for reactivation. In practice, however, the reactivated catalyst lost its activity more rapidly than the original. Therefore, it seems likely that factors other than carbonaceous materials are also involved, such as slight sintering of the oxides and partial formation of metal halides on the surface, all participating in the deactivation. Before application as an industrial catalyst, these problems must be further clarified.

Hydrogenation of CTFE and proposed reaction scheme

It was observed that a fair amount of TFE was formed besides the main product, CTFE, in the reaction over the $NiO-Cr_2O_3$ catalyst. As shown in Table 3, the amount of TFE increased with the reaction temperature, compensating for the decrease in the amount of CTFE. Similarly, the amount of CH_4 increased with a decrease in the amount of CTFE.
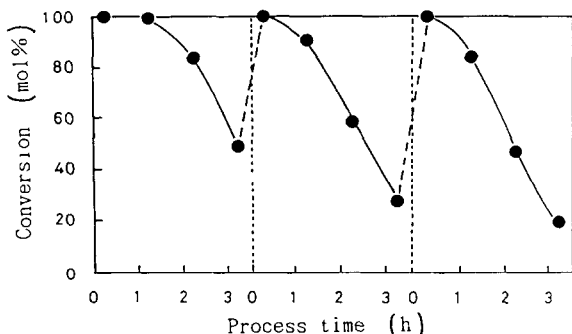

Fig. 7 Effect of successive air oxidation at 600 C for 3 h for reactivation of the 1 1 mixed oxide catalyst. (The hydrodechlorination of CFC-113 was carried out under the same conditions as shown in Table 1)
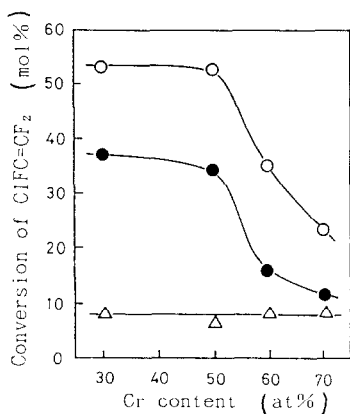
Fig. 8. Effect of the Cr content on total conversion (○), and conversions to CH_4 (●) and TFE (△), of $ClFC-CF_2$ on reaction with H_2. (The reaction conditions were the same as those shown in Table 1 for the hydrodechlorination of CFC-113.)

Thus, it is possible that the CTFE (once formed by the hydrodechlorination of CFC-113) might be further attacked by hydrogen, resulting in the formation of TFE and CH_4. In order to examine this possibility, the hydrogenation of CTFE over mixed oxides containing various amounts of Cr was carried out under the same conditions as applied to the hydrodechlorination of CFC-113. As shown in Fig. 8, TFE and CH_4 were formed as the main products in this hydrogenation. In contrast, the formation of TFE appeared to be unchanged by the Cr content, and the amount of CH_4 decreased remarkably when the Cr content was above 50 at%. This may result from the hydrogenation activity of NiO, which was very high for the hydrogenation of CFC-113 to CTFE, and was modified by the addition of Cr_2O_3.
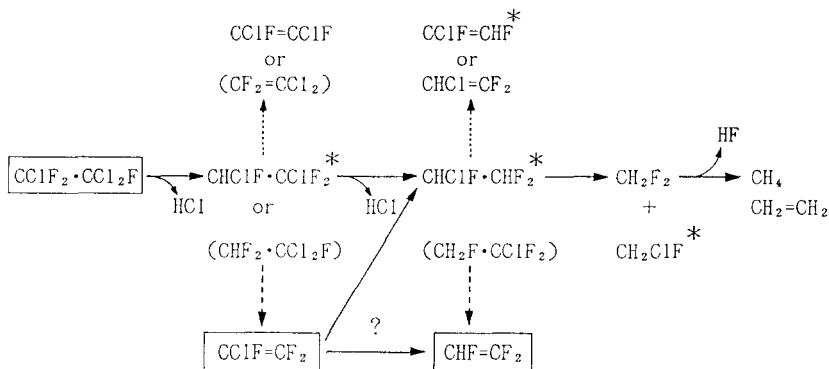

Fig. 9. Proposed reaction scheme: (····→) hydrogenation; (−−−→) dehydrochlorination (−−HCl); (······→) dehydrofluorination (−−HF); (*) unidentified.

Other than TFE and CH_4, a small amount of CH_2F_2 (2–7%) and $H_2C=CH_2$ ($\sim$ 1%), together with a small amount of $HClC=CF_2$, were formed in the hydrodechlorination of CTFE. On the other hand, $C_2Cl_2F_2$, which was formed in a reasonable amount in the hydrodechlorination of CFC-113 (as shown in Tables 1–3), was not found at all in this reaction. Additionally, direct hydrogenation of a vinylic chloride bond (in CTFE) to vinylic hydrogen (in TFE) was difficult at 400 °C, because of the high bond strength of $=C-Cl$ (90 kcal/mol) [6]. Therefore, at the present stage of this study, the reaction scheme shown in Fig. 9 is only one of several possible schemes. Moreover, the presence of intermediate haloethanes, such as $CHClFCClF_2$ and $CHClFCHF_2$, has not yet been confirmed, possibly becuase of their instabilities at higher temperatures especially in contact with metal oxides which may promote dehydrohalogenation.

Acknowledgements

References

1 See, for example, S Okazaki and H Habutsu, *20th Academic Meeting of Union of Chemistry-Related Societies in Chubu Area, Japan, 1989*, Abstr 2H16
2 R Ohnishi, I Suzuki and M Ichikawa, *Chem Lett*, (1991) 841
3 W Ueda, S Tomioka, Y Morikawa, M Sudo and T Ikawa, *Chem Lett*, (1990) 879
4 J W Clark and W V Charlestone, *US Pat 2 685 606* (1953)
5 J II Schofield, *J Electron Spectros Rel Phenom*, *8* (1976) 129
6 N N Samenov, *Some Problems of Chemical Kinetics and Reactivity*, Vol 1, Pergamon, California, 1958, p 16 (Translated by J. E S Bradley)
7 *Powder Diffraction File*, Joint Committee on Powder Diffraction Standards, Philadelphia, PA, 1967