Determination of the kinetics of the reaction of CCl_4 with prefluorided Cr_2O_3 and evaluation of the active site area

A. Farrokhnia, B. Sakakini and K.C. Waugh *

Department of Chemistry, Faraday Building, UMIST, PO Box 88, Manchester M60 1QD, UK
E-mail: ken.waugh@umist.ac.uk

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The reaction of CCl_4 with prefluorided Cr_2O_3 has been studied by temperature-programmed and isothermal methods. Temperature-programmed reaction showed that CCl_3F and CCl_2F_2 were produced simultaneously with activation energies of 64.5 and 62.5 kJ mol^{-1}, respectively, for the surface exchange reaction. It also allowed evaluation of the surface fluoride radius, a value of 1.86 Å being obtained which is slightly higher than the literature value of 1.33 Å. Isothermal reaction at 523 and 673 K of CCl_4 produced simultaneous and instantaneous sharp peaks of CCl_3F and CCl_2F_2. The fluoride ion radius derived from the 523 K experiment was 2.8 Å, suggesting that integration of the peak was terminated prematurely while the value at 673 K was 2.6 Å, suggesting involvement of the subsurface fluorine ions.

KEY WORDS: fluorination; kinetics; chromia; active site area; CCl_4

1. Introduction

The environmental significance of catalysis has never been more evident than in the development of new catalytic processes for the production of 1,1,1,2-tetrafluoroethane (hydrofluoroalkane A134a), the ozone friendly molecule which is the replacement for the ozone destroying molecules dichlorodifluoromethane (A12) and 1,1,1,2,2,-pentafluoro-2-chloroethane (A115). One of the processes developed for the production of A134a involves the fluorination of 1,1,2,2-tetrachloroethane using HF and a Cr_2O_3 catalyst at ~620 K. The most difficult step in this process has been shown to be the fluorination of 1,1,1-trifluoro-2-chloroethane [1].

We have previously investigated the kinetics and mechanism of the reaction of CCl_4 over prefluorided chromium(III) oxide, as a model reaction [2]. The reaction was shown to proceed by a Langmuir–Hinshelwood mechanism, in which a chemisorbed CCl_4 molecule exchanged its chlorine atoms with fluoride ions on the surface of fluorided chromia. Surprisingly also the reaction was shown to proceed by a coincident contemporaneous mono- and di-exchange reaction, forming CCl_3F and CCl_2F_2 in the absence of HF. We explained this by proposing a four-centre intermediate for mono- (intermediate 1) and a dual four-centre intermediate for di-exchange (intermediate 2) where the limiting factor was the number of di-type sites on the surface.

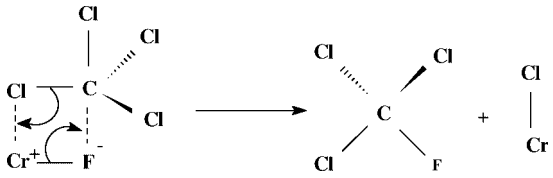
We were able to estimate the number of active sites on the surface (surface fluoride ions), the accuracy of value obtained, however, being compromised by having to deconvolute reaction of the CCl_4 with the surface fluoride exchange reaction from bulk fluoride ions evolving at the surface.

In this study we carried out temperature-programmed reaction experiments to determine the temperature regime within which surface exchange predominated. Having established that, we calculated isothermal exchange reaction in that regime so as to obtain a more accurate estimate of the number of active sites (surface fluoride ions).

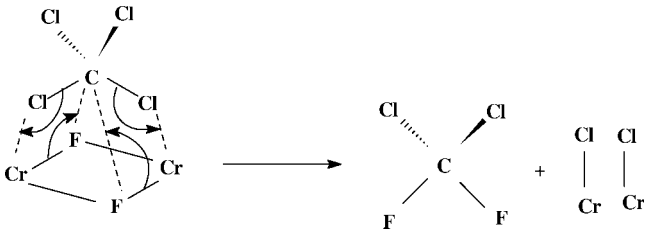
2. Experimental

2.1. Apparatus

The microreactor and gas-handling system have been previously reported [2]. The microreactor is a U-shaped (30 cm long, 0.6 cm ID) Monel microreactor tube, which was connected *via* a heated capillary to an on-line, computer interrogated, mass spectrometer (Hiden Analytical, Warrington,



Intermediate 1. The four-centre intermediate for mono chloro fluoro exchange to form CCl_3F from reaction of CCl_4 with prefluorided chromia catalyst.



Intermediate 2. The intermediate for di-substitution to form CCl_2F_2 from reaction of CCl_4 with prefluorided chromia catalyst.

* To whom correspondence should be addressed.

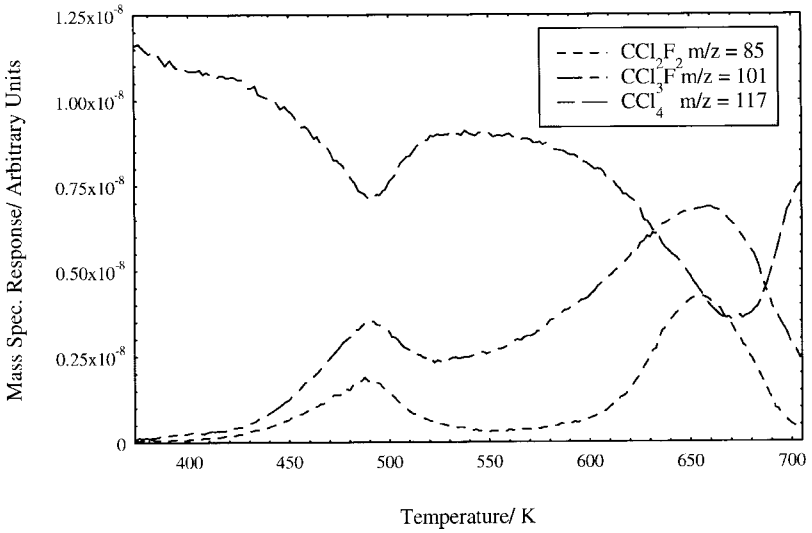


Figure 1. Temperature-programmed reaction of CCl_4 over HF pretreated Cr_2O_3.

England). It is used for temperature-programmed reaction (TPR), temperature-programmed desorption (TPD) in which 16 masses can be followed with temperature/time and *in situ* surface area measurements.

2.2. Catalyst

The catalyst, which was used in this study, is gel chromium oxide. The preparation of this catalyst has been previously described. The calcined chromium(III) oxide was crushed and sieved into particles size of 300–350 μm. The total surface area of the catalyst was determined to be 200 $m^2\,g^{-1}$ by applying the BET method, using N_2, adsorption at 77 K. X-ray diffraction (XRD) of the powder showed that the material contained only amorphous chromium oxide.

2.3. Catalyst pretreatment

The chromium(III) oxide catalyst (~0.2 g) was loaded into the microreactor tube and before any measurement and reaction it was heated under helium (25 $cm^3\,min^{-1}$, 101 kPa) to 623 K and was left at this temperature for 30 min to remove any adsorbed water. The catalyst was then fluorinated *in situ* by 10% HF in He (25 $cm^3\,min^{-1}$, 101 kPa) for approximately 1 h at 623 K. The total amount of HF passed was always 200 cm^3, or 8.2×10^{-3} mol or 2.5×10^{22} fluorine per gram of catalyst. The surface area of the fluoride chromia was measured *in situ* to be 103 $m^2\,g^{-1}$ so that assuming unit reaction probability of the HF with the oxide, this corresponds to a coverage of the oxide with fluoride ions of 1.9×10^{17} ions cm^{-2} which, if the assumption is correct, means that the surface and several layers of the bulk of the Cr_2O_3 have been fluorinated. The catalyst was then sealed and transported to the mass spectrometer.

A CCl_4 mixture (4% CCl_4, 101 kPa) was produced by bubbling He (25 ml min^{-1}, 101 kPa) through liquid CCl_4 held at 273 K.

Table 1
Calculation of fluoride ion radius.

Weight of catalyst	0.127 g
Surface area of catalyst	103 $m^2\,g^{-1}$
Total amount of CCl_3F in the first peak	1.56×10^{-4} mol
Total amount of CCl_2F_2 in the first peak	2.06×10^{-5} mol
Total fluoride removed in the first peak	1.97×10^{-4} mol or 1.19×10^{20} atom F $= 9.15 \times 10^{14}$ atom cm^{-2} $= 1.09 \times 10^{-15}$ cm^2 (atom F)$^{-1}$
Fluoride ion radius	= 1.86 Å

3. Results

3.1. Temperature-programmed reaction of CCl_4 on prefluorided chromia

Figure 1 is the temperature-programmed reaction mass spectrum obtained by passing CCl_4 in He (25 $cm^3\,min^{-1}$, 101 kPa) continuously over HF pretreated Cr_2O_3 while the temperature was increased at a constant rate 5 K min^{-1}. We monitored the rate of reaction of CCl_4 ($m/z = 117$) and production of CCl_3F ($m/z = 101$) and CCl_2F_2 ($m/z = 85$) as a function of temperature.

We suggested [2] that the first peak in the rate of production of CCl_3F and CCl_2F_2 derived from the interaction of CCl_4 with the surface fluoride ions of the catalyst.The validity of this suggestion can be tested by calculating the amounts of CCl_3F and CCl_2F_2 in the first peak of this reaction and show that the fluoride ion radius determined from this is in the range expected for fluorine ions. The amounts of fluoride, calculated from the first peak of CCl_3F and CCl_2F_2, are listed in table 1. The total surface fluoride obtained is 1.19×10^{20} ions, which corresponds to a fluoride ion coverage of 9.15×10^{14} ions cm^{-2} (0.127 g, surface area 103 $m^2\,g^{-1}$), corresponding to an area per fluoride ion of 10.9 $Å^2$ or an ionic radius of 1.86 Å, a value which is in

Table 2
The amount of CCl_3F and CCl_2F_2 formed in the two peaks by temperature-programmed reaction of CCl_4 with prefluorided Cr_2O_3 (0.127 g).

	First peak $T_m = 490$ K	Selectivity[a] (%)	Second peak $T_m = 660$ K	Selectivity (%)
CCl_3F	9.39×10^{19} molecule or 7.39×10^{20} molecule g^{-1}	88.3	2.02×10^{20} molecule or 2.65×10^{21} molecule g^{-1}	92.2
CCl_2F_2	1.24×10^{19} molecule or 9.77×10^{19} molecule g^{-1}	11.7	2.85×10^{19} molecule or 2.24×10^{20} molecule g^{-1}	7.8

[a] Selectivity = product formed/total conversion.

reasonable accord with the quoted value of the fluorine ions radius of 1.33 Å [3]. The higher value for the ionic radius obtained here may be due to the integration/deconvolution but may also be a result of some of area of the surface being occupied by Cr^{3+} ions.

The total amounts of fluorine removed from the catalyst in the second two peaks constitutes 1.97×10^{15} ions cm^{-2} which is around two monolayers of fluorine and so these higher temperature peaks must come from bulk of CrF_3. The total amount of fluorine removed from the catalyst at the end of reaction is 1.65×10^{21} molecule g^{-1} (table 2) which is several times less than the total amount of HF passed over the catalyst in the pretreatment step.

The activation energy for the formation of CCl_3F and CCl_2F_2 from the interaction of chemisorbed CCl_4 with the surface fluoride ion reaction (1) is obtained by line shape analysis of temperature dependence of CCl_3F and CCl_2F_2 peaks at low ($T_m = 490$ K) and high ($T_m = 660$ K) temperature.

$$CCl_4 + F^-_{(s)} \rightleftharpoons CCl_3F + Cl^-_{(s)} \quad (1)$$

The reaction occurs between chemisorbed CCl_4 and the surface F^-, the loss of gas phase CCl_4 upon the production of CCl_3F shows the chemisorbed material to be replenished from gas phase. Assuming the reaction to be first order in CCl_4, the rate of production of CCl_3F is given by

$$\frac{d[CCl_3F]}{dt} = Ae^{-E/RT}[CCl_4][F^-_{(s)}], \quad (2)$$

where $[CCl_4]$, $[CCl_3F]$ and $[F^-_{(s)}]$ are the concentration of each species in units of mol cm^{-3}, A and E are the A factor and activation energy for the exchange reaction. Line shape analysis of the CCl_3F and CCl_2F_2 peaks by the method described previously [2], produces values of 64.5 and 62.5 kJ mol^{-1} for the surface exchange activation energies for the formation of CCl_3F and CCl_2F_2. These values are completely accord with the value which was reported before [3].

The nearly identical value for the activation energy for the mono- and di-exchange is consistent with the postulate of a similar four centre-type complex for both reactions.

3.2. Isotherm time dependence of CCl_4 reaction on a HF pretreated Cr_2O_3 at 523 and at 623 K

Figure 1 shows that the surface reaction forming CCl_3F and CCl_2F_2 occurs at around 450 K with the exchange reaction being completed at 523 K, the bulk exchange reaction occurring at >600 K. Also figure 1 shows that the CCl_3F and CCl_2F_2 are formed simultaneously from CCl_4. To remove the need for deconvolution of the surface exchange reaction from the bulk, the isothermal exchange reactions described below were performed at 523 K, a temperature at which there was negligible bulk F^- ion involvement. A second experiment was calculated at 673 K where significant involvement of the bulk reaction was expected.

The same catalyst (CrF_3) was used for these measurements, *i.e.*, the gel chromium oxide pretreated in a HF/He (10% HF 25 cm^3 min^{-1}, 101 kPa) at 623 K and cooled to room temperature under a He flow (25 cm^3 min^{-1}, 101 kPa). The catalyst was then heated under a He stream (25 cm^3 min^{-1}, 101 kPa) to the desired temperature (523 and 673 K) and maintained here during the reaction with CCl_4. After 2 min the flow was switched to a CCl_4 (4% CCl_4)/He stream (25 cm^3 min^{-1}, 101 kPa) with m/z values 117 (CCl_4), 101 (CCl_3F) and 85 (CCl_2F_2) being followed continuously on the mass spectrometer. The results of these isotherm reactions are shown in figures 2 and 3. Integration of the CCl_3F and CCl_2F_2 peaks was ceased after 2400 s. The amounts of CCl_3F and CCl_2F_2 produced up to this time are reported in table 3.

Several points can be made simply by inspection of the peaks of CCl_3F and CCl_2F_2 in figures 2 and 3, produced by the isothermal reaction of CCl_4 with prefluorided Cr_2O_3. Immediate production of CCl_3F and CCl_2F_2 occurs when the flow is switched to CCl_4/He; this shows unambiguously that the formation of these products occurs with the same kinetics. The CCl_3F and CCl_2F_2 could be formed simultaneously from CCl_4 through the intermediate (intermediate 2). The CCl_4 molecule can also be adsorbed on the CrF_3 with one of the Cl atoms interacting with exposed Cr^{3+} ions (intermediate 1). When the CCl_4 molecule adsorbed with one Cl atom, interacting with one Cr^{3+} ion, the Cl/F exchange reaction can occur through a four-centre intermediate, which would facilitate the breaking of the C–Cl and Cr–F bonds and the formation of the C–F and Cr–Cl bonds.

However, for di-substitution, the CCl_4 molecule adsorbed with two Cl atoms interacting with two chromium ions, al-

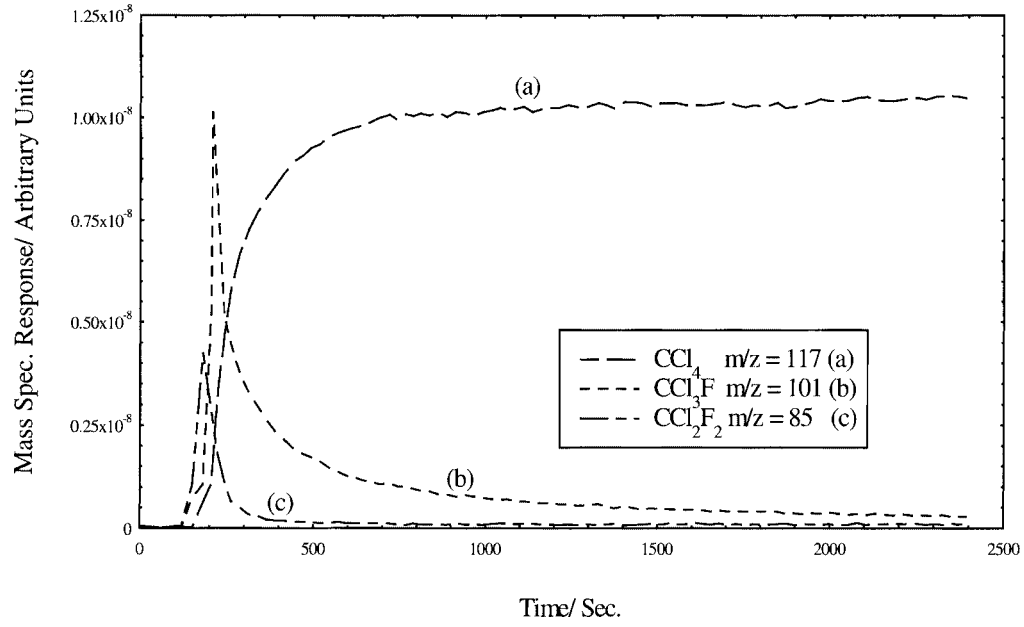


Figure 2. The isothermal reaction of CCl_4 with prefluorided Cr_2O_3 at 523 K.

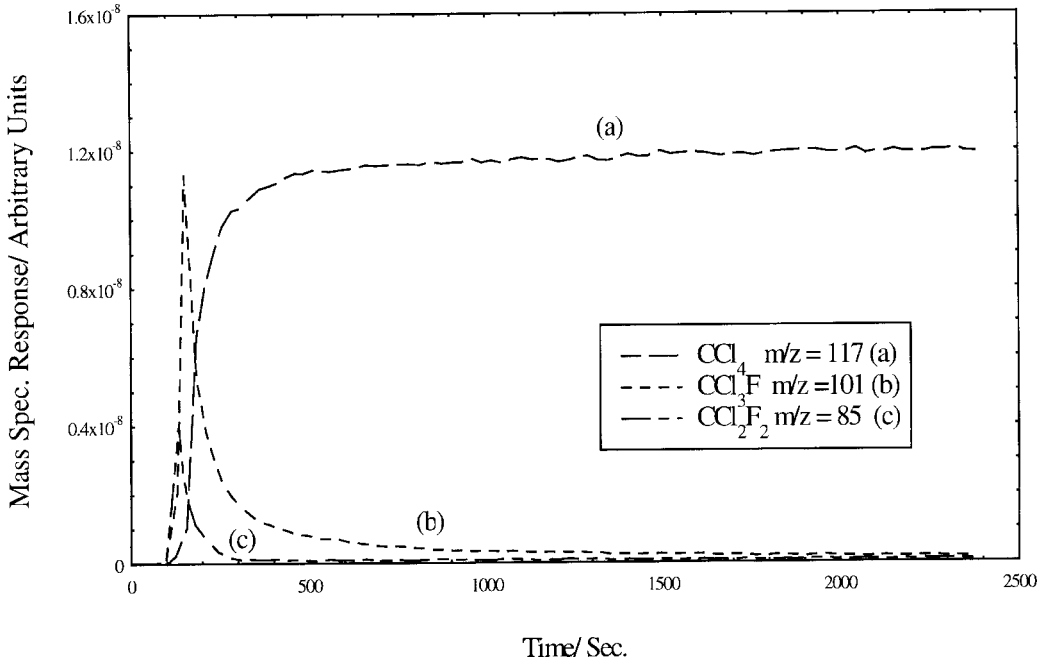


Figure 3. The isothermal reaction of CCl_4 with prefluorided Cr_2O_3 at 673 K.

Table 3
The production of CCl_3F and CCl_2F_2 in the isotherm time-dependent reaction of CCl_4 over prefluorided Cr_2O_3 at 523 and 673 K.

	523 K	Selectivity (%)	673 K	Selectivity (%)
CCl_3F	3.61×10^{19} molecule or 2.84×10^{20} molecule g^{-1}	84.4	4.67×10^{19} molecule or 3.68×10^{20} molecule g^{-1}	85.7
CCl_2F_2	6.68×10^{18} molecule or 5.26×10^{19} molecule g^{-1}	15.6	7.83×10^{18} molecule or 6.16×10^{19} molecule g^{-1}	14.3

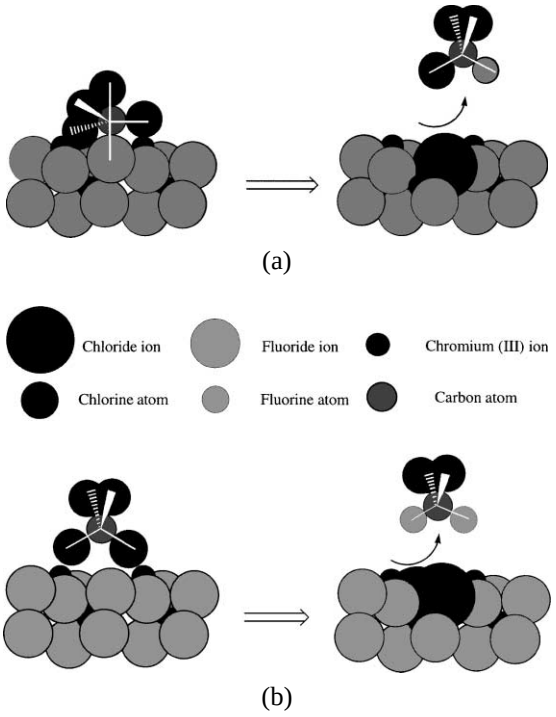


Figure 4. A cut-away model of (001) face of CrF_3 with the adsorbed CCl_4 molecule on it (a) for mono-exchange reaction together with the product CCl_3F and the catalyst after reaction (b) for di-exchange reaction to form CCl_2F_2.

lows simultaneous abstraction of two Cl atoms from the adsorbed CCl_4 molecule and substitution of them by the F of the surface. Figure 4 shows a cut-away model of the (001) face of CrF_3 with a CCl_4 molecule adsorbed on it. (This model is being used here simply to illustrate that the atomic arrangement in CrF_3 does allow for this type of adsorption. It should not be taken to imply that the fluorination of Cr_2O_3 would be considered to produce crystalline CrF_3, only that adsorption site of this type does exist on the CrF_3 surface.)

The total amount of fluoride in the CCl_3F and CCl_2F_2 products at 523 K is 3.9×10^{20} atom g^{-1}. Assuming that this represents complete removal at the surface F^- ions this corresponds to a fluorine ion coverage of 3.85×10^{14} ions cm^{-2} or 2.6×10^{-15} cm^2 (atom F)$^{-1}$. This represents an area of 26 Å ^{2} per fluorine site or a fluorine ion radius of 2.8 Å. This value is higher than produced using the TPR method and is probably a result of arbitrarily ceasing the integration at 2400 s where a small but significant rate of reaction appears to be continuing. Nevertheless, both values show that the catalyst after pretreatment with HF does not produce crystalline CrF_3 (hexagonal close-packed, with the fluorine ion radius of 1.33 Å [3]). XRD also shows that the CrF_3 layer on the Cr_2O_3 is not uniform and probably does contain oxygen both in the bulk and on the surface. Additionally, the rates of isothermal production of CCl_3F and CCl_2F_2 show that after ~1000 s there is a constant ratio of production of both compounds. This is probably due to asymptotic approach completion of the F to Cl exchange on the surface of the catalyst or a fixed rate of diffusion of fluoride ions from the bulk to the surface of the catalyst with a concomitant migration of chloride ions from the chlorided surface of the CrF_3.

The total amount of flouride in the CCL_3 F and CCL_2F_2 products at 673 K is 4.9×10^{20} atom g^{-1}. This is slightly higher than the amount obtained at 523 K, which could result from the release of subsurface fluoride ions. However, the fluoride ion radius calculated from this is 2.6 Å which is only slightly smaller than by 0.2 Å, the value obtained at 523 K. Both values however are larger than the literature values of the fluoride ion radius which is 1.33 Å. This results from the surface of the catalyst not simply consisting of close-packed fluoride ions. A given amount of the area will be occupied by chromium ions and possibly oxygen ions from incomplete O^{2-}/F^- exchange during the HF pretreatment.

Another point of note in relation with isothermal reaction and TPR is that the selectivity to CCl_3F is always higher than that to CCl_2F_2. This is probably due to the low surface population of the two neighbouring Cr^{3+} sites required for the adsorption of the CCl_4 molecule through two Cl^- ions.

References

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