CH$_3$CF$_{3-n}$Cl$_n$ haloalkanes and CH$_2$=CF$_{2-n}$Cl$_n$ halo-olefins on γ-alumina catalysts: reactions, kinetics and adsorption

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Abstract

The heterogeneously catalyzed reactions of the haloalkane, CH$_3$CF$_{3-n}$Cl$_n$, and halo-olefin, CH$_2$=CF$_{2-n}$Cl$_n$, series have been studied on a γ-alumina catalyst and the experimental results compared with calculated thermodynamic data. The main reactions occurring in this system can be explained by the following reaction paths: dehydrohalogenation, hydrohalogenation, F/Cl and Cl/F exchange with hydrogen halides. Dismutation reactions which are observed in other halocarbon series are unimportant in this system. A survey of the dominant reactions is given. In addition, the kinetic behaviour of CH$_3$CF$_2$Cl on the γ-alumina catalyst and the adsorption of various halocarbons have been investigated. The isosteric enthalpies of adsorption demonstrate that the interaction between the haloalkanes and the solid surface is more dominant than simple condensation.

Keywords: Chlorofluorocarbons; γ-Alumina catalysts; Heterogeneous catalysis; Kinetics; Adsorption; Enthalpy of adsorption

1. Introduction

Haloalkanes of the CH$_3$CF$_{3-n}$Cl$_n$ series are not only possible substitutes for perhalogenated refrigerants but they are of value in polymer chemistry. Thus, CH$_3$CF$_2$Cl is an intermediate in the production of vinylidene fluoride, CH$_2$=CF$_2$, while the latter is used as a monomer in polymerization or copolymerization processes.

Hofmann and coworkers [1,2] have investigated the heterogeneously catalyzed dehydrochlorination of CH$_3$CF$_2$Cl using NiCl$_2$ as the catalyst in a kinetic study. Two competitive reactions forming CH$_2$=CFCl and CH$_3$CF$_3$ were also discussed. Other studies have been concerned with the determination of the kinetic parameters of various reactions [3,4], e.g. the dehydrofluorination of CH$_3$CF$_3$.

Winfield et al. [5] have studied the reactions between solid AlCl$_3$ and CH$_3$CCl$_3$ or CH$_2$=CCl$_2$ and have also undertaken infrared spectroscopic studies. These reactions are accompanied by the formation of a purple oligomeric material on the solid surface. The behaviour of CH$_3$CCl$_3$ on γ-Al$_2$O$_3$ chlorinated with CCl$_4$ or OCCl$_2$ has been reported by Thomson et al. [6] who showed that strong Lewis acid sites were formed after activation. Chlorine-36 tracer studies indicated that the chlorine associated with these Lewis sites is unaffected by the dehydrochlorination of CH$_3$CCl$_3$. In contrast,

the chlorine associated with Brönsted sites undergoes ^{36}Cl exchange with HCl. A reaction scheme proposed for the dehydrochlorination of CH$_3$CCl$_3$ includes the adsorption of CH$_3$CCl$_3$ and CH$_2$CCl$_2$ on the Lewis acid sites while HCl is adsorbed on the Brönsted acid sites. The model suggests that in the initial stage the dehydrochlorination of CH$_3$CCl$_3$ is reversible, although CH$_2$CCl$_2$ also reacts to give a purple chlorine-containing material on the surface of the catalyst.

A further paper reported the catalytic room-temperature fluorination of CH$_3$CCl$_3$ with HF using a γ-alumina catalyst fluorinated with sulphur tetrafluoride [7]. Further details on this work were reported by Thomson et al. [8]. The SF$_4$-activated γ-alumina was conditioned with CH$_3$CCl$_3$, CH$_2$CCl$_2$ or other chlorocarbons, the products obtained from CH$_3$CCl$_3$/HF mixtures being CH$_3$CCl$_2$F, CH$_3$CClF$_2$, CH$_3$CF$_3$ and CH$_2$CCl$_2$, for example. Olefins such as CH$_2$CClF and CH$_2$CF$_2$ were not formed under the conditions employed. Moreover, the fluorination of starting materials such as CCl$_4$ or CHCl$_3$ was not observed. Obviously, the ability of a chlorocarbon to undergo Lewis acid-catalyzed dehydrochlorination or oligomerization reactions appears to be precondition for room-temperature fluorination [8].

Ballinger et al. [9] have studied the degradation of CH$_3$CCl$_3$ over γ-alumina within the temperature range 300–1000 K under flow conditions. At temperatures above 400 K, an α,β-HCl elimination reaction forming CH$_2$=CCl$_2$ and HCl

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occurs. Total decomposition was observed at temperatures greater than 700 K, with heavy carbon deposition on the alumina and HCl formation. Chloroacetylene was not obtained, indicating a kinetic barrier to this reaction.

An infrared spectroscopic study [10] has confirmed that Lewis acid sites are responsible for the dehydrochlorination of CH_3CCl_3, with surface Al—OH groups not being involved in this reaction. Further details regarding Lewis acidity and heterogeneous halogen exchange are given elsewhere [11]. Generally, the authors have identified only some of the reactions occurring in this system and did not take other competitive and side-reactions into consideration.

In this present study, we have surveyed hydrohalogenation and dehydrohalogenation processes and halogen-exchange reactions with hydrogen halides. Such a survey was based on the investigation of every reactant with the $CH_3CF_{3-n}Cl_n$ (haloalkane) and $CH_2{=}CF_{2-n}Cl_n$ (halo-olefin) series in the absence and presence of hydrogen chloride and hydrogen fluoride, respectively. These reactions are catalyzed and influenced by the solid surface, and since adsorption is the initial step in the reaction pathway, it is necessary to take into consideration the adsorption behaviour of the respective halocarbons. The catalyst employed was γ-alumina. In previous studies, we have investigated the properties of this catalyst as applied to other haloalkane reactions. The catalyst contains Lewis as well as Brönsted acid sites [11–14].

In all cases, the experimental behaviour is compared with thermodynamic predictions. Such data are only rarely available and obviously not always comparable. For this reason, we have calculated the thermodynamic data using the PM3 model [15] with the help of a computer program. It was tested by comparing the calculated data for the $CHF_{3-n}Cl_n$ series with literature data. Good agreement ($\pm 5\%$) was observed in all cases. Here, we present only the principal results; further details and numerical values have been reported in Ref. [16].

2. Experimental details

γ-Alumina (300 mg; specific surface area, 180 m^2 g^{-1}; size range, 160–315 μm; bulk density, 0.58 g cm^{-3}) was dried by means of a nitrogen stream (flow reactor) at 300 °C for 30 min. It was then preactivated with the respective halocarbon at 300 °C for 20 min at a flow rate of 0.2 mmol min^{-1} (CH_3CCl_3, 0.33 mmol min^{-1}; CH_2CCl_2, 1.25 mmol min^{-1}). After preactivation the catalyst contained 2–14 wt.% fluoride (depending on the particular halocarbon employed) and <0.5 wt.% chloride. X-Ray phase data and ESCA measurements have been reported previously [14]. Preactivation with fluorine-free chlorohydrocarbons resulted in a higher chloride content (0.5–2 wt.%).

After preactivation, the product distribution was determined as follows. The preactivated catalyst was first heated to 100 °C, then treated with the particular halocarbon and after a short period of equilibration (final activation) the product composition analyzed. The catalyst was then purged with dry nitrogen once more and heated up to the next temperature. The results were reproducible provided the temperature did not exceed 300 °C. Long treatments at higher temperatures led to a partially irreversible change in catalyst (coke deposits).

A constant gaseous halocarbon flow was established by using a flow meter (UCAR) (fluorochemicals from Fluorochem Limited). With liquid halocarbons [CH_3CCl_3 and $CH_2{=}CCl_2$ (Merck)], a constant stream of nitrogen was allowed to flow through a bottle containing the particular halocarbon. Continuous HCl and HF flow rates were adjusted by means of Monel needle valves and, in the case of HCl, controlled by calibrated rotameters. HCl (Messer-Griesheim) was dried with $Mg(ClO_4)_2$. The flow of HF (Merck) was controlled by means of a thermostatted manometer and periodical alkaline absorptions. Both the halocarbon and hydrogen halide flows were mixed and introduced into a vaporizer located just before the inlet of the flow reactor. All gas tubing was heated to prevent condensation.

The composition of the gas phase at the exit of the reactor (atmospheric pressure) was determined by gas chromatography (column: Poraplot U; i.d., 0.53 mm; length, 25 m; FID and ECD detectors). For the determination of side-products, FT-IR/GC coupling (Perkin-Elmer system 2000) and GC/MS were applied.

Kinetic measurements were carried out in a similar flow reactor (catalyst weight, 30 mg). The residence time t_r was defined as the ratio of the catalyst bulk volume to the volumetric rate of flow. It was varied by changing the gas volume flow. Measurements were carried out in the Henry region of the adsorption isotherm.

The isotherms were determined using an ASAP 2000 Accelerated Surface Area and Porosimetry system (Micromeretics) that had been modified for operation at various temperatures. The experimental error involved in the determination of the isosteric enthalpy of adsorption did not exceed $\pm 5\%$.

3. Results

3.1. Principal reactions on fluorinated γ-alumina
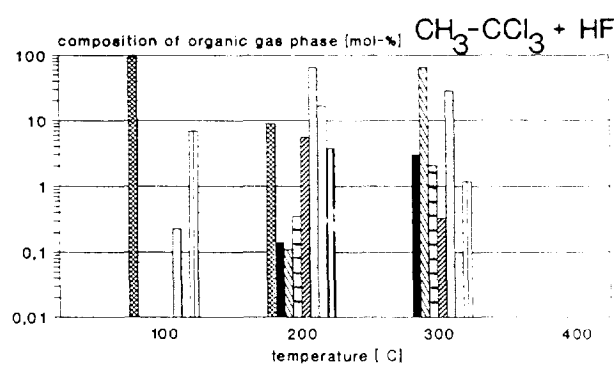
3.1.1. CH_3CCl_3

In the system investigated, dehydrochlorination is mostly favoured thermodynamically above 150 °C [16]. Fig. 1(a) shows the experimentally determined compositions at various temperatures (note the logarithmic scale which has been introduced to enable better recognition of lower concentrations). The principal product was $CH_2{=}CCl_2$ with acetic acid as a side-product formed by the hydrolysis of carbon–halogen bonds. Obviously, the catalyst contained a considerable number of OH groups which led to the formation of hydrolysis products.
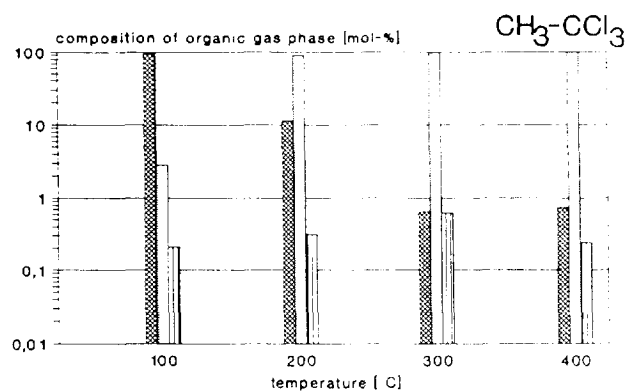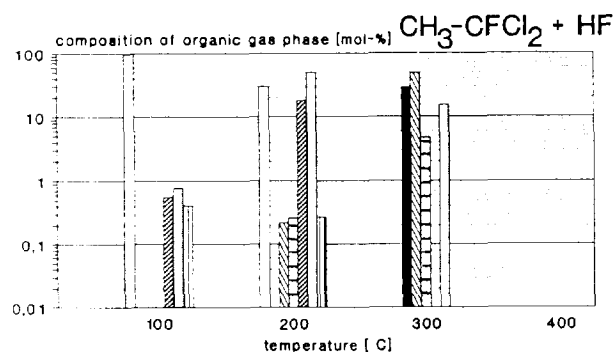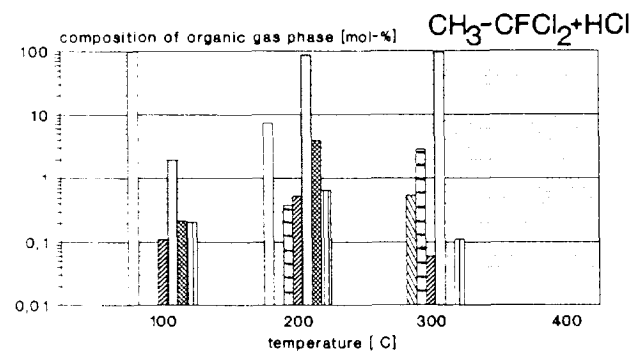
(a)
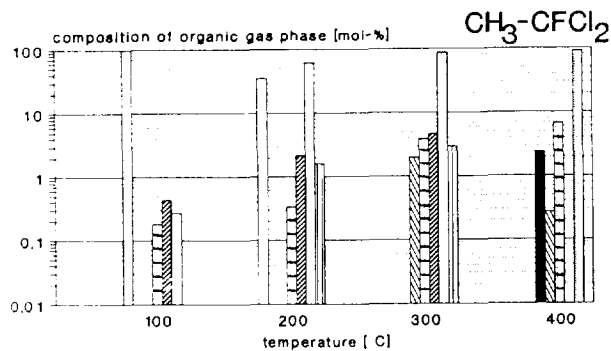
(a)

(b)

(b)

Fig. 1. Product distribution with temperature, starting substance CH₃CCl₃. Conditions (a) 0.33 mmol min⁻¹ CH₃CCl₃, 0.5 l h⁻¹ nitrogen; (b) 0.33 mmol min⁻¹ CH₃CCl₃ + 1.17 mmol min⁻¹ HF (ratio 1:3.5), 3 l h⁻¹ nitrogen.

3.1.2. CH₃CCl₃ + HF

The F/Cl exchange, forming CH₃CFCl₂ and HCl, is endothermic over the temperature range within which CH₃CCl₃ is stable [16]. The formation of CH₃CFCl₂ did not occur at 100 °C [Fig. 1(b)]. If a sufficient concentration of CH₂=CCl₂ was present, then CH₃CFCl₂ and its higher fluorinated derivatives were obtained (200 °C). At higher temperatures, CH₃CFCl₂ is unstable and other consecutive products were observed.

3.1.3. CH₃CFCl₂

As may be concluded from our thermodynamic calculations [16], dehydrofluorination is the reaction to be expected with CH₃CFCl₂ at temperatures above 300 °C. This reaction is coupled with the consecutive formation of AlF₃. Hence, the preference for dehydrofluorination has been increased further. Obviously, this is the reason for CH₂=CCl₂ being the principal product even at 200 °C [compare Fig. 2(a)]. At 100 °C, small amounts of F/Cl exchange product CH₃CF₂Cl were observed. Dismutation, which was also favoured at lower temperatures, did not occur.

(c)

Fig. 2. Product distribution with temperature, starting substance CH₃CFCl₂. Conditions: (a) 0.2 mmol min⁻¹ CH₃CFCl₂, 3 l h⁻¹ nitrogen; (b) 1.25 mmol min⁻¹ CH₃CFCl₂ + 1.17 mmol min⁻¹ HF (ratio 1:0.93), 3 l h⁻¹ nitrogen; (c) 1.25 mmol min⁻¹ CH₃CFCl₂ + 2.33 mmol min⁻¹ HCl (ratio 1:1.87), 1 l h⁻¹ nitrogen.

The product distribution at 300 °C and 400 °C was influenced by consecutive reactions involving CH₃CF₂Cl and CH₂=CCl₂; CH₃CFCl₂ was unstable under these conditions.

3.1.4. CH3CFCl2 + HF

A higher HF concentration in the system led to an increase in the F/Cl exchange products CH_3CF_2Cl and CH_3CF_3 [see Fig. 2(b))]. Dehydrofluorination was slightly repressed in this case.

3.1.5. CH3CFCl2 + HCl

The addition of HCl led to the formation of slight amounts of CH_3CCl_3 [see Fig. 2(c)]. A reaction pathway via $CH_2=CCl_2$ is assumed.

3.1.6. CH3CF2Cl

Dehydrochlorination is normally more favoured than dehydrofluorination in this system [16]. However, in our studies, the opposite was observed [$CH_2=CFCl$ formation, see Fig. 3(a)]. The reason is probably associated with the coupled formation of Al–F bonds leading to a change in the thermodynamics. Hydrogen fluoride can react to form CH_3CF_3 as is favoured thermodynamically. The formation of $CH_2=CCl_2$ can be explained by a Cl/F exchange on $CH_2=CFCl$.

3.1.7. CH3CF2Cl + HF

In a similar manner to the behaviour of CH_3CFCl_2, the F/Cl exchange reaction is increased by the addition of HF [see Fig. 3(b)]. For this reason, CH_3CF_3 is the main product.

3.1.8. CH3CF2Cl + HCl

This reaction is impossible thermodynamically [16] as confirmed by experiment [Fig. 3(c)]. The difference between the behaviour of pure CH_3CF_2Cl and that on addition of HCl is the increase in $CH_2=CCl_2$ formation. In this case, $CH_2=CCl_2$ cannot be the dehydrofluorination product of CH_3CFCl_2 because the latter is not observed, although it would be stable up to 200 °C. Instead, the following reaction pathway is assumed (cf. the appropriate section):

$$CH_2=CFCl + HCl \longrightarrow CH_2=CCl_2 + HF \qquad (1)$$
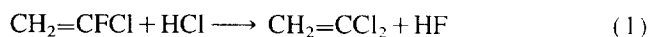
3.1.9. CH3CF3

As may be deduced from thermodynamics [16] dehydro-fluorination is expected at higher temperatures. The results depicted in Fig. 4(a) confirm this conclusion experimentally.

3.1.10. CH3CF3 + HCl

In this case, Cl/F exchange does not play an important role. Fig. 4(b) demonstrates the existence of only traces of CH_3CF_2Cl at 200 °C and $CH_2=CFCl$ at 300 °C.

3.1.11. CH2=CCl2 + HCl

The addition of HCl is favoured thermodynamically up to 150 °C [16] and a corresponding CH_3CCl_3 content was determined at lower temperatures [see Fig. 5(a)]. The reaction is reversible.
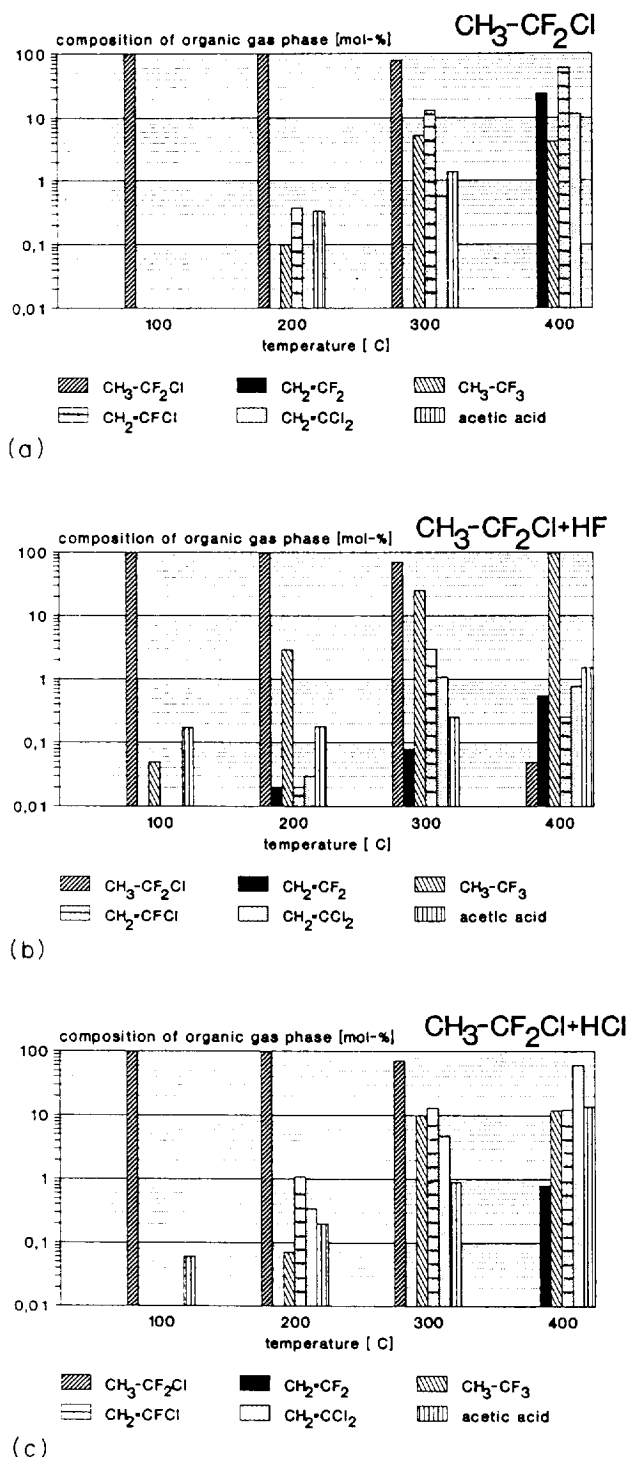

Fig. 3. Product distribution with temperature, starting substance CH_3CF_2Cl. Conditions: (a) 0.2 mmol min^{-1} CH_3CF_2Cl, 3 l h^{-1} nitrogen; (b) 0.2 mmol min^{-1} $CH_3CF_2Cl + 1.17$ mmol min^{-1} HF (ratio 1:5.83), 3 l h^{-1} nitrogen; (c) 0.2 mmol min^{-1} $CH_3CF_2Cl + 2.33$ mmol min^{-1} HCl (ratio 1:11.7), 1 l h^{-1} nitrogen.

3.1.12. CH2=CCl2 + HF

The addition of HF is also expected thermodynamically [16]. The first step is the formation of CH_3CFCl_2 (reversible reaction), which is observed at 100 °C [Fig. 5(b)]. Consec-
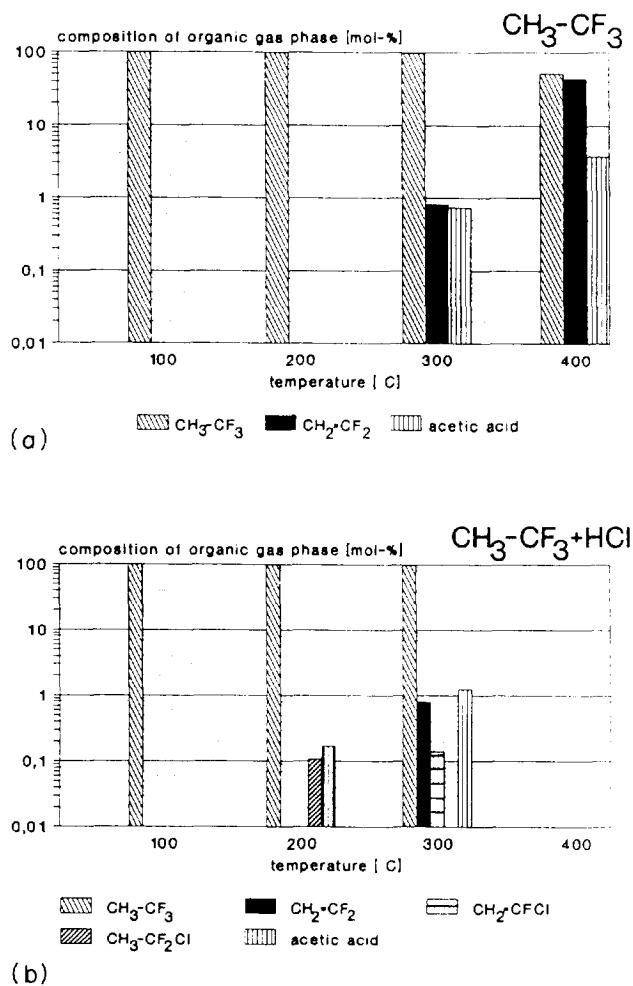
(a)

(b)

Fig. 4. Product distribution with temperature, starting substance CH_3CF_3. Conditions: (a) 0.2 mmol min^{-1} CH_3CF_3, 3 l h^{-1} nitrogen; (b) 0.2 mmol min^{-1} CH_3CF_3 + 0.083 mmol min^{-1} HCl (ratio 1:0.42), 0.5 l h^{-1} nitrogen.

utive F/Cl exchange leads to the formation of CH_3CF_2Cl and CH_3CF_3 at higher temperatures.

3.1.13. $CH_2=CFCl$

The addition of HF is favoured up to 200 °C. At higher temperatures, a dismutation forming $CH_2=CF_2$ and $CH_2=CCl_2$ and a Cl/F exchange forming $CH_2=CCl_2$ are possible [16]. Fig. 6(a) shows the experimental results using pure $CH_2=CFCl$. The HF addition product could be detected at 200 °C and 300 °C; the reaction is reversible.

The question arises as to where did the HF come from? Obviously, a slight decomposition of the starting substance still occurs with HF and HCl being released and adsorbed on the catalyst surface. Hence CH_3CF_2Cl may be formed by fluorination of non-degraded starting substance with HF, followed by consecutive reactions of the product.

The presence of both $CH_2=CF_2$ and $CH_2=CCl_2$ can be explained by dismutation, but other pathways cannot be excluded.

3.1.14. $CH_2=CFCl + HF$

According to thermodynamics, CH_3CF_2Cl should appear up to 300 °C from HF addition. Consecutive F/Cl exchange forming CH_3CF_3 was also observed.

3.1.15. $CH_2=CFCl + HCl$

Fig. 6(c) shows that formation of the HCl addition product, CH_3CFCl_2, did not occur. Instead, Cl/F exchange forming $CH_2=CCl_2$ took place.

3.1.16. $CH_2=CF_2 + HF$

The addition of HF is favoured thermodynamically in this system, followed by HCl addition [16]. Fig. 7(a) illustrates the experimental results obtained. At higher temperatures, the stability of CH_3CF_3 decreased since the equilibrium was shifted towards the starting substances.

3.1.17. $CH_2=CF_2 + HCl$

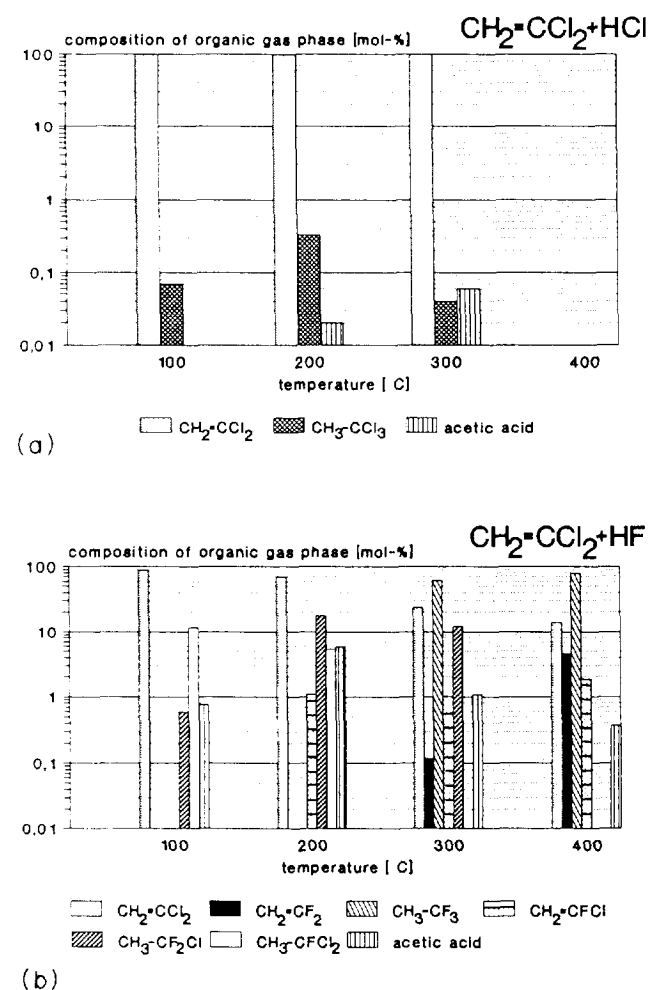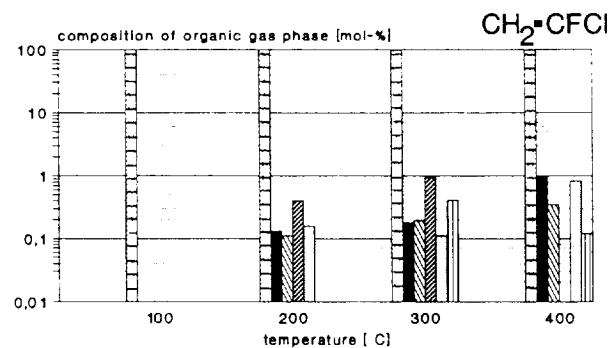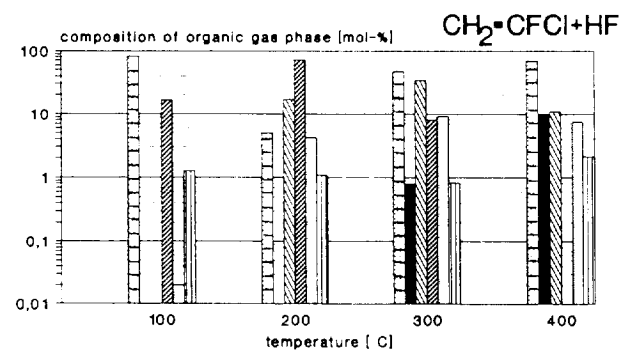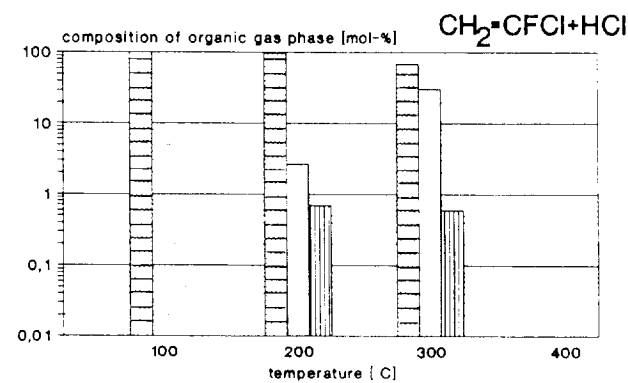The column at 100 °C in Fig. 7(b) represents the composition of the starting substance which contained a slight

(a)

(b)

Fig. 5. Product distribution with temperature, starting substance $CH_2=CCl_2$. Conditions: (a) 1.25 mmol min^{-1} $CH_2=CCl_2$ + 0.083 mmol min^{-1} HCl (ratio 1:0.07), 0.5 l h^{-1} nitrogen; (b) 1.25 mmol min^{-1} $CH_2=CCl_2$ + 1.17 mmol min^{-1} HF (ratio 1:0.93), 3 l h^{-1} nitrogen.
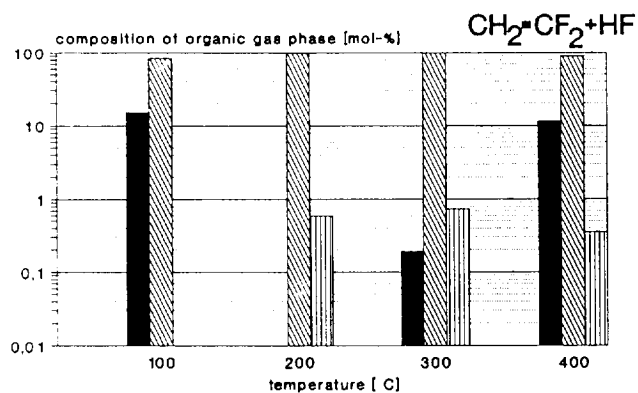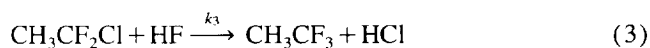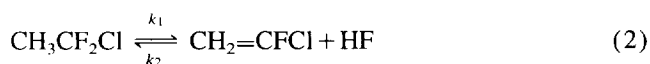
(a)

(b)

(c)

Fig. 6. Product distribution with temperature, starting substance CH_2=CFCl. Conditions: (a) 0.2 mmol min^{-1} CH_2=CFCl, 3 l h^{-1} nitrogen; (b) 0.2 mmol min^{-1} CH_2=CFCl + 1.17 mmol min^{-1} HF (ratio 1:5.8), 3 l h^{-1} nitrogen; (c) 0.2 mmol min^{-1} CH_2=CFCl + 2.33 mmol min^{-1} HCl (ratio 1:11.7), 1 l h^{-1} nitrogen.

amount of CH_3CF_3. No reaction occurred at this temperature. At higher temperatures the HCl addition product, CH_3CF_2Cl, appeared but had disappeared at 400 °C as a result of consecutive reactions.
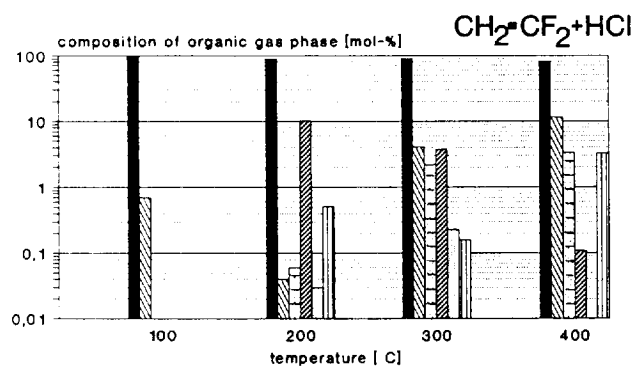
3.2. Kinetics

From the variation in the residence time, it is possible to draw conclusions about the mechanism of the reaction under certain circumstances. For example, the existence of concentration maxima indicate intermediates which are formed in an initial step and then undergo further reaction in the next step. Figs. 8(a)–(c) show the variation with residence time of the concentration of the various reaction products, using as an example the CH_3CF_2Cl reactions at different temperatures. As can be seen, maxima do not occur and, hence, intermediates could not be identified.

However, from kinetic modelling it was possible to show that the following reactions gave the best fit to the experimental data:

$$CH_3CF_2Cl \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_2=CFCl + HF \qquad (2)$$

$$CH_3CF_2Cl + HF \overset{k_3}{\longrightarrow} CH_3CF_3 + HCl \qquad (3)$$

(a)

(b)

Fig. 7. Product distribution with temperature, starting substance CH_2=CF_2. Conditions: (a) 0.2 mmol min^{-1} CH_2=CF_2 + 1.17 mmol min^{-1} HF (ratio 1:5.8), 3 l h^{-1} nitrogen; (b) 0.2 mmol min^{-1} CH_2=CF_2 + 0.083 mmol min^{-1} HCl (ratio 1:0.42), 3 l h^{-1} nitrogen (the product distribution at 100 °C corresponds to the composition of the starting substance).
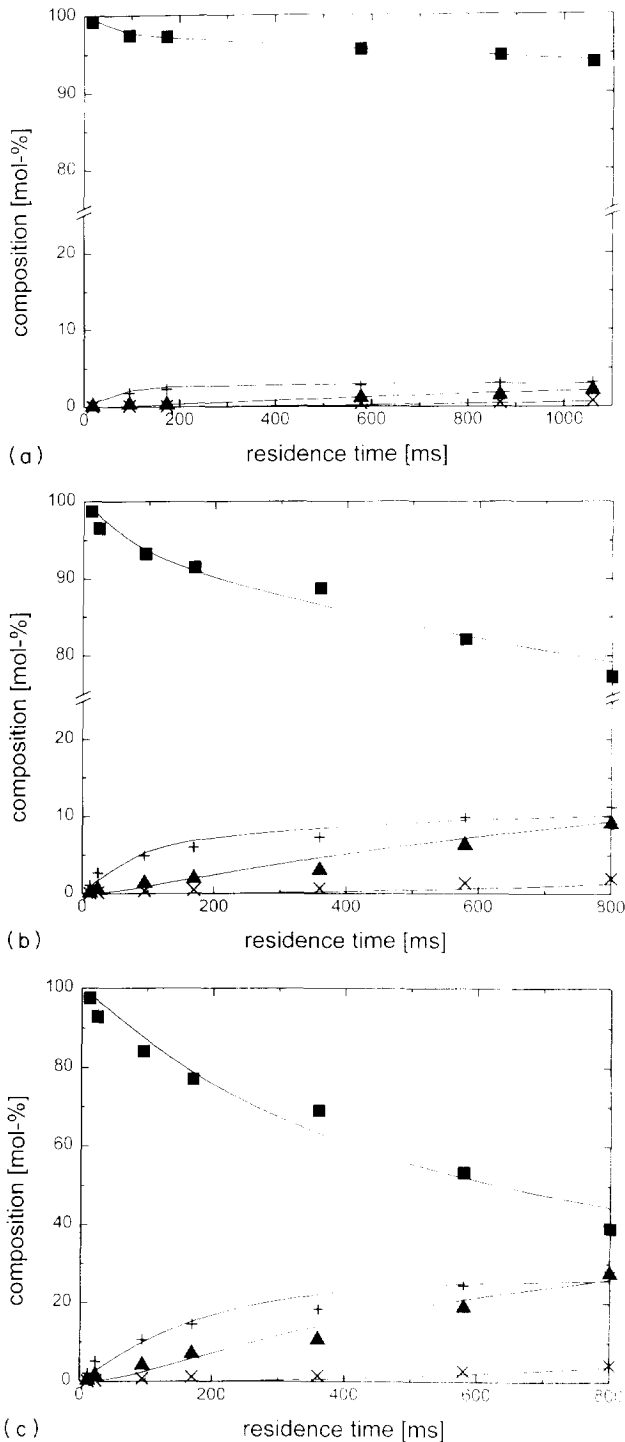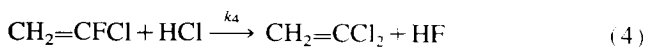
(a)

(b)

(c)

residence time [ms]

Fig. 8. Comparison of the calculated and experimental course of the reaction (starting substance CH₃CF₂Cl) where the concentrations of the various reactants and products are depicted as: ■, CH₃CF₂Cl; △, CH₃CF₃; +, CH₂=CFCl; and ×, CH₂=CCl₂ at (a) 300 °C, (b) 350 °C and (c) 400 °C, respectively.

$$CH_2=CFCl + HCl \xrightarrow{k_4} CH_2=CCl_2 + HF \qquad (4)$$

The model on which this scheme is based was derived from the experimental data. The formation of acetic acid as a side-product was disregarded.

Fig. 8(c) shows that for the reactant CH_3CF_3 in particular, some divergence between the experimental and calculated variation in concentration does occur. Eq. (3) above suggests that CH_3CF_3 is formed as a consecutive product (increasing slope of the curve), whereas the experimental data indicate primary product formation (decreasing slope). This means that either the rate of CH_3CF_2Cl fluorination is much faster than the rate of HF desorption, or that the fluorinated solid surface directly reacts with CH_3CF_2Cl.

3.3. Adsorption of halocarbons on fluorinated γ-alumina

The product distribution observed experimentally is not always identical with the thermodynamically expected product distribution. Some deviations may be explained by subsequent Al—F bond formation, but not all. Obviously, the influence of adsorption gives rise to certain preferences in the reaction pathway (kinetic reasons). For this reason, the adsorption isotherms of the $CH_3CF_{3-n}Cl_n$ and $CH_2=CF_{2-n}Cl_n$ halocarbon series on fluorinated γ-alumina have been determined. As an example, Fig. 9 shows the isotherms obtained with CH_3CF_2Cl and demonstrates that with increasing temperature the isotherms approach the linear behaviour expected from Henry's law. To obtain a better understanding of the different adsorption properties of the various halocarbons, it is useful to compare their respective isosteric enthalpies of adsorption (see Fig. 10). The halo-olefins $CH_2=CF_2$ and $CH_2=CFCl$ exhibit an isosteric enthalpy of adsorption which is comparable with the appropriate enthalpy of vaporization [17,18]. Hence, there is no significant attractive contribution beyond that of simple condensation. On the other hand, there is an increase in interaction between the fluorinated alumina and the haloalkanes CH_3CF_3 and CH_3CF_2Cl. Their isosteric enthalpies of adsorption are significantly higher than the enthalpies of vaporization. Unfortunately, the enthalpies of vaporization for CH_3CFCl_2 and $CH_2=CFCl$ were not available and the determination of adsorption data
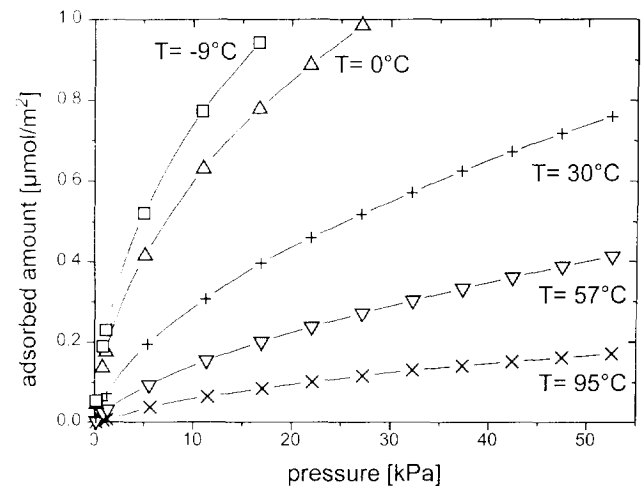

pressure [kPa]

Fig. 9. Adsorption isotherms of CH_3CF_2Cl on fluorinated γ-alumina at various temperatures.

isosteric enthalpy of adsorption (kJ/mol)

enthalpy of vaporization ...... 0.31 μmol/m² coverage
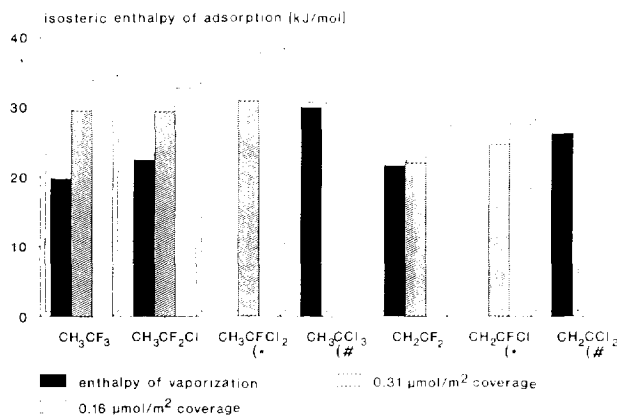0.16 μmol/m² coverage

Fig. 10. Isosteric enthalpies of adsorption at different coverages compared with the respective enthalpies of vaporization (taken from Refs. [17,18]): * enthalpy of vaporization not available; # adsorption data not measurable.

for CH_3CCl_3, $CH_2=CCl_2$, HF and HCl was not possible with our instrument. Hence, it is at this stage not yet possible to distinguish numerically between the influence of adsorption kinetics and the surface reaction itself.

Kohne [19] has reported the following isosteric enthalpies of adsorption for the similar β-CrF_3/HF system: 35 kJ mol^{-1} at 6 μmol m^{-2} coverage of HF and 59 kJ mol^{-1} at 2 μmol m^{-2} coverage of the same adsorbate, while the enthalpies of adsorption for the $CF_{4-n}Cl_n$ halocarbons lie within the range 20–35 kJ mol^{-1} (being independent of coverage over a particular temperature interval). In our system, i.e. halocarbon/ fluorinated γ-Al_2O_3, we have obtained enthalpies of adsorption between 22 kJ mol^{-1} and 31 kJ mol^{-1} at 0.31 μmol m^{-2} coverage. Due to selective adsorption on the strongest sites, the enthalpies of adsorption increase as the coverage diminishes (26–37 kJ mol^{-1} at 0.16 μmol m^{-2}, cf. Fig. 10). Values above 60 kJ mol^{-1} can be expected for the enthalpies of adsorption of HF and HCl. The significantly stronger interaction with the solid surface implied can be confirmed by temperature-programmed desorption [11].

4. Discussion

Fig. 11 presents a survey of the main reactions occuring on an activated γ-alumina catalyst which may be resolved by

variation of temperature and starting substance. The reactions have been subdivided into dominant reactions, secondary reactions and those that could not clearly be resolved. Nevertheless, there are, of course, differences in reactivity among reactions in the same category.

Obviously, dismutations do not play an important role. This is in contrast to the behaviour of the $HCF_{3-n}Cl_n$ series [12,13]. In the reactions studied here, all the products can be explained in terms of hydrohalogenations, dehydrohalogenations and halogen-exchange reactions with hydrogen halides. The reason for the absence of dismutations is that other reactions are more thermodynamically favoured. Steric factors may also play a part.

Fig. 11 also illustrates that fluorination of CH_3CCl_3 (with CH_3CF_3 being the desired product) proceeds as follows. The monofluorinated product, CH_3CCl_2F, is obtained via CH_2CCl_2, whereas the difluorinated CH_3CClF_2 is obviously formed via direct F/Cl exchange between HF and the monofluorinated product. There is some evidence that the trifluorinated CH_3CF_3 is also produced without formation of CH_2CF_2 formation as an intermediate. These results are comparable with those obtained for the '130' $CCl_{3-n}F_nCH_2(Cl,F)$ series [19,20]. In that particular system, the final fluorination step obviously proceeded via F/Cl exchange with HF instead of dehydrochlorination and subsequent hydrofluorination (with olefins as the intermediate). In their consideration of the fluorination of CH_3CCl_3, Thomson et al. [8] also reported that the formation of CH_3CCl_2F can be most obviously described by a dehydrochlorination followed by a hydrofluorination, since CH_2CCl_2 is always observed as a coproduct. On the other hand, dehydrochlorination/hydrofluorination processes are regarded as less credible for the consecutive fluorination steps leading to CH_3CClF_2 and CH_3CF_3. This is in agreement with our results (cf. Fig. 11).

A comparison with the scheme for the reactions of CH_3CClF_2 on $NiCl_2$ proposed by Müller and Hofmann [2] shows several differences, possibly due to the different catalyst employed. Thus, the dehydrofluorination of CH_3CClF_2 may be regarded as being an almost irreversible reaction. In
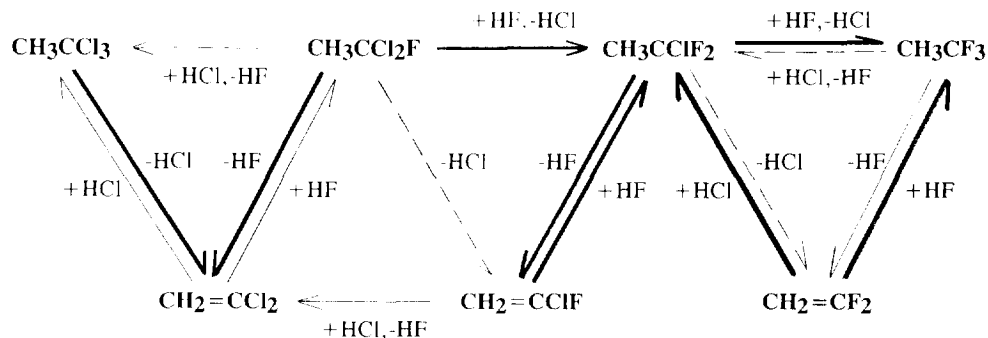

Fig. 11. A survey of the observed reactions occurring in the $CH_3CF_{3-n}Cl_n$ and $CH_2=CF_{2-n}Cl_n$ series (thick line: dominant reaction; thin line: secondary halocarbon reaction; dotted line: reactions which could not be clearly resolved).

contrast, we have observed that the hydrofluorination of $CH_2=CClF$ proceeds readily. Equally, we have confirmed the convient F for Cl exchange of CH_3CClF_2 to form CH_3CF_3. Ethynes and radical reactions occur at temperatures above 400 °C and for this reason they are not assumed to be reactive intermediates in the system of main reactions presented here. Ballinger et al. [9] have also reported that no evidence exists for the production of chloroacetylene from $CH_2=CCl_2$. For a detailed discussion of the side-reactions occurring, including coke formation processes, we refer the reader to Refs. [11,14,16].

From the kinetic results, it may be assumed that a number of consecutive reaction steps occur within the surface layer of adsorbed halocarbons. Thus, the intermediates present undergo further reaction instead of being desorbed. Consequently, a complex kinetic behaviour is observed. The nature of the interaction between the halocarbons and the solid surface is more than simple condensation. As can be seen from Fig. 10, there is an increase in the enthalpies of adsorption with decreasing coverage, indicating that the strongest sites are occupied first. Such adsorption has an important influence on the product distribution. Thus, whereas for the reaction of CH_3CF_2Cl dehydrochlorination would be expected from thermodynamics, dehydrofluorination is observed to be the main reaction occurring [see Fig. 3(a)]. Obviously, there is stronger interaction between the fluorine atom (relative to chlorine) of the adsorbed haloalkane and a Lewis acid site on the solid surface [11] leading to the experimentally observed reaction pathway. Adsorption of the haloalkane molecule is assumed to be the reason for the observed 'deviation' from thermodynamics.

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