

Heterogeneous catalyzed decomposition reactions of dichlorodifluoromethane in the presence of water on γ -alumina

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Abstract

The heterogeneous catalyzed decomposition of CCl_2F_2 (CFC-12) in the presence of water was investigated, employing γ -alumina as catalyst. The catalyzed hydrolysis reaction yields very high conversion degrees of CFC-12 in the first reaction stage. For a period of about 3 h there is a remarkable lack of balance between the amount of liberated HF and HCl owing to the uptake of HF by the oxide solid forming α - AlF_3 . Only after about 3 h does the heterogeneous solid/gas reaction come to an end and then the HCl and the HF balance is equal. With the increasing fluoride content of the solid phase, the decomposition degree of CFC-12 decreases to a stable value of about 60% with respect to liberated CO_2 . The conversion degree of CFC-12 seems to be higher but this is owing to the formation of CClF_3 (CFC-13), which is nearly stable under the conditions used. Mechanistic explanations are given for the formation of CClF_3 whether by dismutation reactions or owing to hydrofluorination reactions of CFC-12. Arguments are given about which mechanism might be the most probable. Furthermore, mechanistic hypotheses are concluded and discussed with respect to the processes at the catalyst surface on the basis of the experimental results.

Keywords: Difluorodichloromethane; Catalytic destruction; Alumina catalysts; Mechanisms

1. Introduction

The elimination of chlorofluorocarbons (CFCs), which have been implicated in atmospheric ozone depletion, was mandated by the Montreal Protocol. Although the total CFC phaseout for the industrialized countries was in 1993, under the industrial treaty developing countries are allowed to continue producing CFCs for 10 years beyond the deadline. The alternative compounds, the hydrofluorocarbons (HFCs), which are considered to have nearly no ozone depleting potential, are already in production. Since the production of CFCs will still be continued in a number of developing countries and since large amounts of CFCs are still being used in the economy today, there is a demand to develop new techniques to destroy these compounds after use. Owing to their wide industrial use as refrigerants and propellants, the destruction of CFC-11 and CFC-12 is of particular interest.

Up to now the common procedure has been the burning of CFCs, which is, of course, very energy intensive. Catalytic destruction could be an interesting alternative to this process and can be realized by various methods.

Thus, especially during the last few years the catalytic decomposition of a series of CFCs was investigated extensively.

The destruction of CFC-11 [1] or of CFC-12 in the presence of different gases such as H_2O [2] and NH_3 [3,4], was investigated on a large scale using solid catalysts. Additionally, the destruction of other halocarbons such as tetrachlorodifluoroethane (CFC-112) and trichlorotrifluoroethane (CFC-113) in the presence of ethanol was studied by Miyatani et al. [5]. For the hydrodechlorination of CFC-113 Ueda et al. [6] found NiO as the most effective solid. The decomposition of chlorotrifluoromethane (CFC-13) and some other CFCs in the presence of water vapor [7] or hydrocarbons [8] showed that Fe_2O_3 /carbon in the first case and γ -alumina in the second case were the most active catalysts. The authors found that the conversion of CFCs decreases with the increasing fluorine number in the molecule, $\text{CFC-113} > \text{CFC-114} > \text{CFC-115}$, owing to the higher stability of the carbon-fluorine bond. Imamura et al. [9] found that various acid catalysts, e.g. zeolites, silica-alumina, titania-silica were deactivated rapidly during the decomposition of CFC-12 owing to the formation of inorganic fluorides. Therefore, a BPO_4 catalyst [10] was tested with regard to its stability against CFC-12 attack. A phosphate-zirconia catalyst [11] which had a superacid nature gives 100% conversion of CFC-

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12 at lower temperatures of about 573 K. During the oxidative destruction of CFC-11 and CFC-12 on various Y-zeolites and titania solid fluorides, i.e. TiOF_2 , were formed which are responsible for deactivating the catalysts [12,13]. Furthermore, the authors found the presence of water more effective for oxidative destruction than oxygen.

In order to get a deeper view on the mechanistic aspects of this kind of reaction this paper focusses on the investigation into the destruction mechanism of CFC-12 on γ -alumina surfaces. The main aim was to understand the processes happening at the solid surface as well as in the gas phase. Although all compounds, CFC-11, CFC-12 and CFC-113, are the major ozone depleting compounds which have been produced in the past, in this work exclusively the Cl-halocarbons CFC-12 and indirectly CFC-11 were used as gaseous reactants in order to obtain general information about the destruction processes of the gas phase. Detailed studies were carried out to investigate the stability of the catalyst used. By employing several techniques, changes in the acidity on the solid surface were monitored in order to compare them with the catalytic activity and the mechanistic changes observed.

2. Experimental

2.1. Catalytic reactions

The catalyzed hydrolysis reactions of CFC-12 were carried out under atmospheric pressure using a gas flow reaction apparatus (see Fig. 1). The flow reactor made of nickel

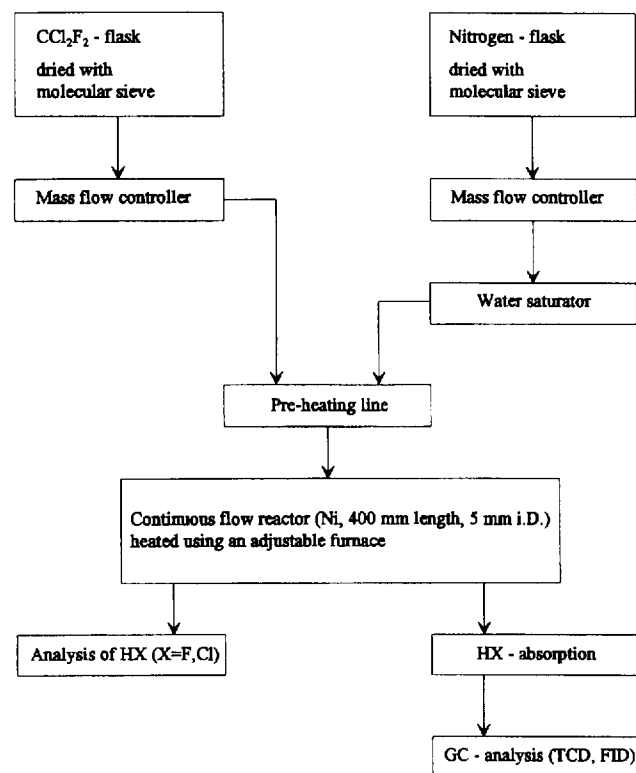


Fig. 1. Scheme of the apparatus used for catalytic decomposition reactions.

(length 400 mm, inner diameter 5 mm) was heated using an adjustable electric furnace. As catalyst a commercial γ - Al_2O_3 was used. The pellets were crushed and sieved to 250–500 μm . The surface area of this solid was 255.2 $\text{m}^2 \text{g}^{-1}$. For each reaction 750 mg of the alumina catalyst was charged in the reactor on a nickel-sieve. Before starting the reaction, the catalyst was calcined at 673 K in a pre-dried nitrogen gas stream (gas flow: 19.8 ml min^{-1}) for 1 h. After drying, the reaction temperature was fixed and a constant gas flow containing adjusted amounts of CFC-12, water, and nitrogen passed through the catalyst. Nitrogen and CFC-12 were held constant by a gas flow controller. The constant nitrogen stream was passed through a saturator with distilled water heated to a constant temperature. CFC-12 and nitrogen/water were then mixed and put into the reactor.

The residence time t_r was estimated using the following equation:

$$t_r = \frac{\text{free volume of the catalyst bed } [\text{cm}^3]}{\text{gas flow of all components } [\text{cm}^3 \text{ s}^{-1}]}$$

2.2. Analysis of the gaseous products

The analysis of the reaction products CFCs, CO, and CO_2 was carried out chromatographically. For the analysis of the CFCs a gas chromatograph, MGC 4000 from Chromatron (carrier gas: nitrogen, 1.7 l h^{-1} ; packed column: 2 m 10% OV 101 on Chromosorb W, HP, 80–100 mesh; detector: FID), was used. The CO_2 and CO were analyzed using a gas chromatograph, HP 5890 (carrier gas: hydrogen, 30 ml min^{-1} ; packed column: 2 m carbon molecular sieve, 80–100 mesh; detector: TCD).

The acidic gases HX (HF and HCl) were determined by absorption in 1 molar NaOH for 2.5 min and were titrated using 0.5 molar H_2SO_4 . Additionally, the concentrations of fluoride and chloride were separately determined from these solutions by ion-sensitive electrodes.

2.3. Characterization of the solid catalysts

The alumina catalysts were characterized before and after reaction by XRD, by determination of the surface areas and the fluoride contents.

To analyze the fluoride contents the solid samples were melted with KNO_3 and then transformed in an apparatus according to Seel [14], employing a water vapor distillation. The free fluoride contents were determined with a fluoride sensitive electrode calibrated for the concentration range concerned (relative error 4.0%).

The solid surface areas were determined using the surface analyzer Micromeritics ASAP 2000 by the BET method (relative error 0.1%).

The XRD measurements were carried out using an X-ray diffractometer XRD 7 Seiffert-FPM.

2.4. FT-IR photoacoustic measurements

The determination of the nature of the acidic surface sites was carried out by means of FT-IR photoacoustic measurements (Perkin-Elmer, system 2000).

70 mg of the catalyst sample were placed in a reactor. The sample was heated at 423 K in a constant nitrogen gas flow of 50 ml min⁻¹. Then the adsorption of pyridine (30 μl pulse) was carried out. After an isothermal period of 15 min, the sample was cooled to room temperature and transported to the photoacoustic cell in order to determine the IR spectrum. The wave numbers of the characteristic bands are 1440 cm⁻¹ for Lewis sites (corresponding to coordinatively adsorbed pyridine), 1540 cm⁻¹ for Brønsted sites (corresponding to pyridinium ion), and 1490 cm⁻¹ for both sites.

2.5. Suitable experimental conditions

As in the case of catalytic dismutation reactions [15,16], for catalytic hydrolysis reactions there is a temperature region where the process slowly starts, this being between 573 and 673 K. At 773 K satisfyingly high conversions were obtained and only a small change was observed at higher temperatures. However, there is clear evidence that at about 973 K pyrolysis reactions begin in addition to catalyzed hydrolysis.

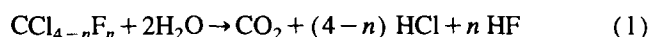
Another influence on the conversion degree of a heterogeneous solid–gas reaction is the dependence on the residence time of the gas phase used. It was found that these processes can be disregarded by using residence times higher than about 1 s.

To sum up, from these pre-investigations the following experimental conditions were concluded: residence time (t_r) = 3 s, temperature (T) = 773 K.

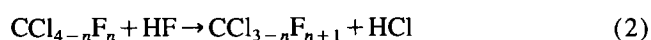
3. Results

3.1. The catalytic decomposition reactions

From the thermodynamic point of view, the hydrolysis reaction in the presence of water according to Eq. (1) is to consider:



As is shown in Table 1, the free reaction enthalpies for these hydrolysis reactions are negative for all chlorofluoromethanes, clearly indicating the thermodynamic possibility of these reactions. The same situation can be found for chlorine–fluorine exchange reactions according to Eq. (2):



as well as for dismutation reactions, as is shown for the CCl_{4–n}F_n series in Eq. (3):

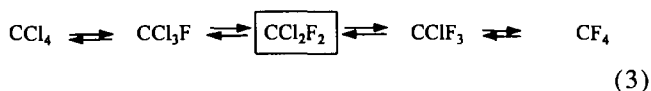


Table 1
Thermodynamic calculations for the given reactions

Reaction	$\Delta_R G_{773\text{K}}^\circ$ (kJ mol ⁻¹)
Hydrolysis	
$\text{CCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{HCl}$	-396.3
$\text{CCl}_3\text{F} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{HCl} + \text{HF}$	-385.1
$\text{CCl}_2\text{F}_2 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{HCl} + 2\text{HF}$	-368.2
$\text{CClF}_3 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{HCl} + 3\text{HF}$	-316.5
$\text{CF}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{HF}$	-284.7
Dismutation	
$2\text{CCl}_3\text{F} \rightarrow \text{CCl}_4 + \text{CCl}_2\text{F}_2$	-5.7
$2\text{CCl}_2\text{F}_2 \rightarrow \text{CCl}_3\text{F} + \text{CClF}_3$	-34.8
$2\text{CClF}_3 \rightarrow \text{CCl}_2\text{F}_2 + \text{CF}_4$	19.9
Hydrofluorination	
$\text{CCl}_4 + \text{HF} \rightarrow \text{CCl}_3\text{F} + \text{HCl}$	-11.2
$\text{CCl}_3\text{F} + \text{HF} \rightarrow \text{CCl}_2\text{F}_2 + \text{HCl}$	-16.9
$\text{CCl}_2\text{F}_2 + \text{HF} \rightarrow \text{CClF}_3 + \text{HCl}$	-51.7
$\text{CClF}_3 + \text{HF} \rightarrow \text{CF}_4 + \text{HCl}$	-31.8

In the latter cases as well, the free reaction enthalpy values are negative (see Table 1) but the reactions start only if a suitable catalyst and a certain temperature are used. The hydrolysis reaction of CFCs exhibits the same demand as reactions 2 and 3, catalytic activation is needed in order to make the reaction kinetically possible.

According to Eq. (1) there are several opportunities to monitor the hydrolytic conversion of CCl₂F₂ whether by observing the decrease in the CFC themselves, or the formation of CO₂, HF or HCl, respectively. In Fig. 2(a) the dependence of the CCl₂F₂ conversion on the reaction time is given by monitoring the concentrations of CFC-12 and the concentrations of CO₂ with the time. As can be seen, up to a reaction time of about 100 min nearly 100% conversion of CCl₂F₂ can be obtained, but certain amounts of CClF₃ are formed additionally. It can be observed that in the very first stage of the reaction, a nearly complete conversion of CCl₂F₂ to CO₂ occurs, followed by a rapid decrease in CO₂ formation while CCl₂F₂ continues to disappear. It is interesting that just as the CO₂ concentration decreases, the formation of CClF₃ starts. Obviously, the conditions on the surface have been changed remarkably, owing to a heterogeneous reaction between the gaseous CCl₂F₂ and the alumina surface. Only small changes occur during the next period until after about 240 min another strong jump in the concentration lines is observable. Again there is a decrease in the CO₂ concentration, accompanied by a further increase in unconverted CCl₂F₂ as well as the reaction product CClF₃. After this, no changes of the conversion degree or the selectivity were observed in any reactions, indicating that the changes on the surface of the solid had been completed by this point at the latest.

A deeper understanding of the chemical changes occurring during this period is possible if one compares the concentration versus the time curves of the liberated hydrogen halides which are given in Fig. 2(b). Generally, both curves should be equal owing to the same molar ratios of both halogens in a CCl₂F₂ molecule and should be 50% for every hydrogen

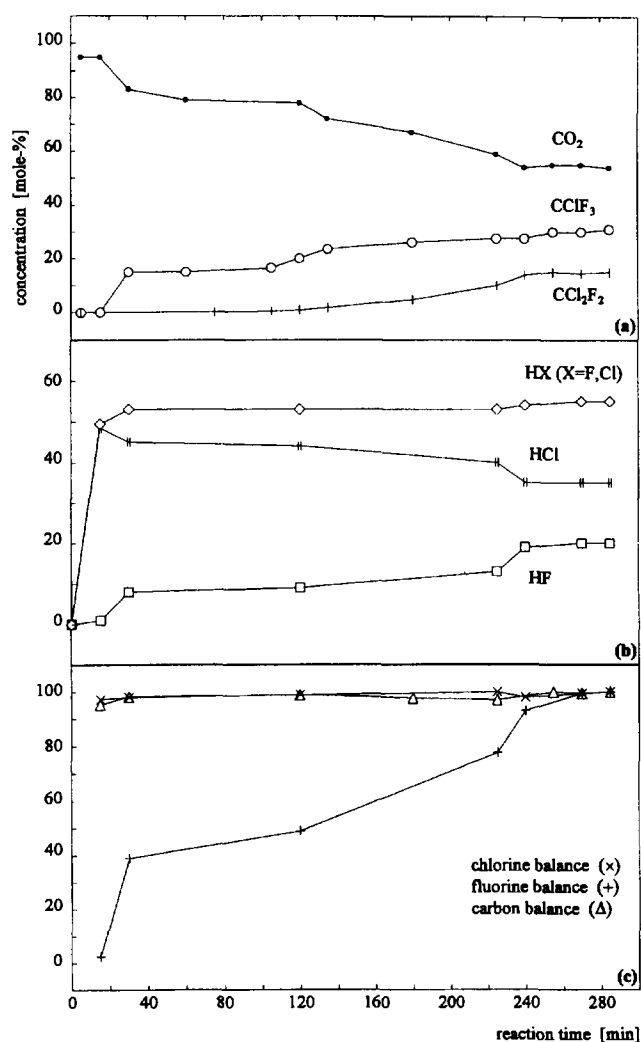


Fig. 2. Decomposition of CFC-12 with water on calcined γ -alumina at 773 K (residence time: 3 s). (a) Distribution of the carbon containing products in the gas phase. (b) Mole balances of HF, HCl, and the sum of hydrogen halides. (c) Mole balances of fluorine, chlorine, and carbon.

halide in the case of a complete hydrolysis. In fact, there are strong differences between the hydrogen halides. Whereas the HCl concentration at the very beginning is of the theoretical value, at that time there is no HF detectable in the gas phase. At the same time as the first strong decrease in the conversion of CCl_2F_2 was observed (Fig. 2(a)), we found a slow decrease in HCl, but a sudden increase in HF. After this,

these conditions are nearly stable up to the next strong decrease in the conversion of CCl_2F_2 in the range of 220 to 240 min where the overall conversion decrease is again accompanied by a slow decrease in HCl and an increase in HF in the gas phase. Further on there are stable relations without any changes in the concentrations of the reactants. Note that there is always a discrepancy between the amounts of HCl and HF detected in the gas phase even then, which is in contrast to the expectations according to Eq. (1).

For this reason, in Fig. 2(c) the overall fluorine and chlorine balances have been established by adding all the halogen in the organic compounds and in the hydrogen halides. This has been done separately for the chlorine and fluorine balance as well as for the carbon balance. The amounts are given in relative values compared to 100% of the theoretical possible amount of the considered elements. As is shown in Fig. 2(c) there is nearly a 100% carbon balance (haloalkanes plus CO_2) and chlorine balance (HCl and chlorine in the haloalkanes) over the whole reaction time. However, surprisingly, at the same time there is a very strong mismatch between the calculated and experimentally determined fluorine balance. It is striking that after the last point of change in the conversion degree at about 240 min, all discrepancies disappear and stable catalytic conditions are established.

Consequently, probable changes in the solid phase were investigated. The main results of these investigations are given in Table 2. The X-ray results reveal a permanent fluorination of the starting alumina until after 270 min the solid phase mainly consists of α - AlF_3 with traces of γ - Al_2O_3 . The fluoride contents in the solid confirm this but also indicate that to a certain extent X-ray amorphous phases are also formed (10.3% F^- after 10 min but no X-ray indications!). If the solid is exposed to the gas phase for long enough a nearly complete conversion to AlF_3 can be observed after 270 min. Nevertheless, even after 24 h only α - AlF_3 can be detected by X-ray. The changes in the chemical composition are accompanied by a decrease in the surface area from 255.2 $\text{m}^2 \text{g}^{-1}$ at the beginning to 12.5 $\text{m}^2 \text{g}^{-1}$ at the end.

As a result, the lack of the fluorine balance in the gas phase discussed above can be explained by the intake of fluoride in the solid. Owing to the nearly complete conversion of the solid phase to aluminium fluoride after about 240 min (the last strong change in the concentration curves) the intake of

Table 2
Characterization of the catalyst used for catalytic decomposition of CFC-12 with water on γ -alumina

Reaction time (min)	XRD detected phases	Surface area ($\text{m}^2 \text{g}^{-1}$)	Fluoride content (mass%)
0	γ - Al_2O_3	255.2	0
5	γ - Al_2O_3	223.6	9.5
10	γ - Al_2O_3	191.9	10.3
30	γ - Al_2O_3 and traces of α - AlF_3	141.4	13.3
60	γ - Al_2O_3 and traces of α - AlF_3	85.7	16.5
120	Equal amount of γ - Al_2O_3 and α - AlF_3	21.1	19.3
270	α - AlF_3 and γ - Al_2O_3 as minor phase	13.8	27.5
1440	α - AlF_3	12.5	32.5

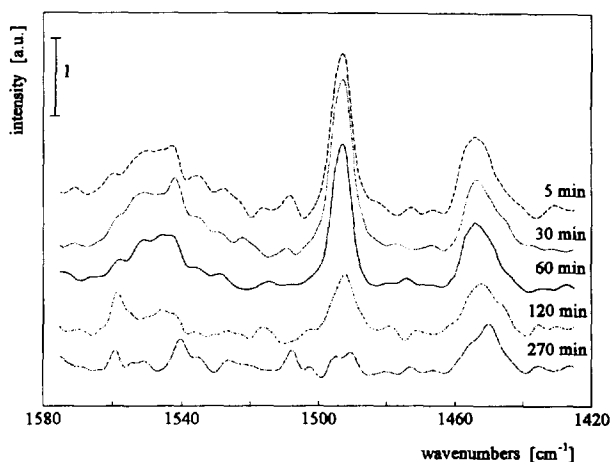


Fig. 3. Photoacoustic measurements depending on the reaction time.

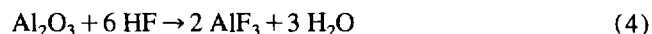
fluoride by the solid is small, consequently resulting in the accordance of all elemental balance curves in the ideal 100% region.

TPD and FT-IR-photoacoustic measurements were carried out (Fig. 3) in order to monitor probable changes of the surface acidity as a result of the fluorination of the solid. The peaks at 1545 cm^{-1} are characteristic only of Brønsted acidic sites, the peaks at 1490 cm^{-1} represent both Brønsted and Lewis acidic sites, and the ones at 1450 cm^{-1} represent only Lewis acidic sites on the surface. As a result of the fluorination of the solid the Lewis acidity of the surface seems to be unchanged, whereas the Brønsted acidity decreases. As a result of FT-IR measurements using NH_3 as probe molecule we found a decrease in the Lewis acidity up to about one third from the untreated, only calcined alumina to the fluorinated alumina catalyst (after 270 min), whereas the Brønsted acidity completely disappeared.

4. Discussion

4.1. The conditioning period of the $\gamma\text{-Al}_2\text{O}_3$ used

According to Eq. (1) the molar ratio of the hydrogen halides to carbon dioxide formed during the catalyzed decomposition of CCl_2F_2 should be $4n_{\text{CO}_2} = n_{\text{HX}}$. In fact this equation is distorted up to 270 min of reaction time. The amounts of HCl should be the same as HF ($n_{\text{HCl}} = n_{\text{HF}}$) if a complete reaction occurs. Even taking into consideration the fact that part of the fluorine is bonded in CFC-13, there is a mismatch in the fluorine balance of the gas phase. The reason for this lack of HF is obviously a consecutive reaction with alumina according to Eq. (4):



Owing to this reaction, the HF formed during the hydrolysis reactions is trapped by the solid oxide, resulting in a distortion of the expected molar balance of gaseous reaction products. In agreement with this, a permanent increase in the fluoride content of the solid alumina can be detected

(Table 1). The same reaction pathways could be observed during the conditioning period of alumina as well as chromia catalysts for dismutation or isomerization reactions of CFCs [16] or HFCs [17], respectively. From the latter measurements it is known that among the different modifications of AlF_3 only $\beta\text{-AlF}_3$ is highly catalytically active, whereas $\alpha\text{-AlF}_3$ is completely inactive [18]. X-ray measurements reveal the formation of $\alpha\text{-AlF}_3$ exclusively in our reaction system, which is somewhat surprising considering the catalytic activity observed. On the contrary, the TPD and pyridine photoacoustic measurements reveal less acidity on the catalyst surface formed after 270 min, which is in accordance to that which would be expected for inactive $\alpha\text{-AlF}_3$. It is to be noted that the peak in the region between 1445 and 1455 cm^{-1} in Fig. 3 provides evidence of the presence of two different acidic sites (maximum at 1455 cm^{-1} and another one at 1445 cm^{-1}). The slightly fluorinated samples have a peak maximum at 1455 cm^{-1} with only a small shoulder at about 1445 cm^{-1} (e.g. after 30 min). In contrast, the highly fluorinated samples reveal their maximum at lower wave numbers with only a small shoulder at 1455 cm^{-1} (e.g. samples after 270 min).

Similar peaks of the photoacoustic spectra have been observed in case of magnesium doped $\beta\text{-AlF}_3$ phases [19]. Here, with increasing Mg content of the $\beta\text{-AlF}_3$, similar changes of the peaks with a small shoulder were observed, finally leading to a complete loss of the catalytic activity at about 50% Mg. It is not entirely clear to us what this second type of centre might be, but we assume a destructive interaction of two different kinds of acidic sites, resulting in a nearly complete loss of the catalytic activity.

Consequently, both $\alpha\text{-AlF}_3$ and $\beta\text{-AlF}_3$, were checked separately as catalysts for this hydrolysis reaction. As can be seen in Fig. 4, $\alpha\text{-AlF}_3$ exhibits almost negligible activity which is in full agreement with the results presented in Ref. [18]. On the contrary, $\beta\text{-AlF}_3$ reveals comparatively high activity at the beginning which decreases with the reaction

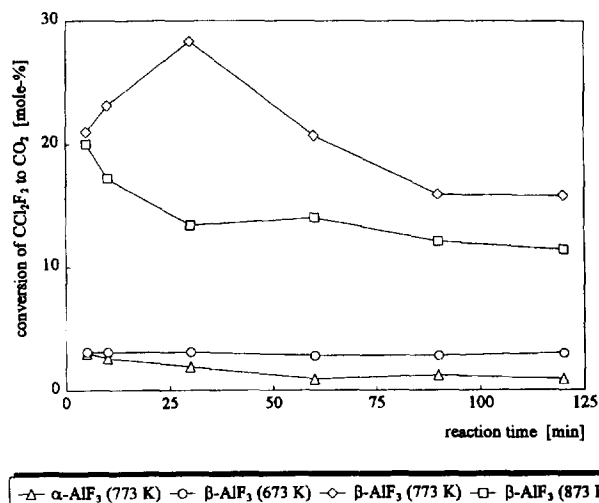


Fig. 4. Decomposition of CFC-12 with water on $\alpha\text{-AlF}_3$ and $\beta\text{-AlF}_3$ (residence time: 3 s).

time owing to phase transformation of β -AlF₃ to α -AlF₃ at these temperatures, as shown by X-ray measurements.

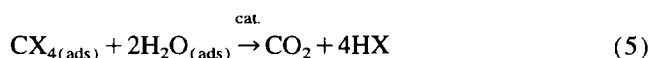
It is probable that the fluoride phases formed on γ -alumina surface during the conditioning period are

1. crystalline α -AlF₃ with a very strong disturbed surface and additionally X-ray amorphous parts of β -AlF₃, or
2. another explanation is that, owing to the permanent water content in the gas phase and the high temperatures used, partial hydrolysis reactions of the surface aluminium fluoride occur, forming in a reversible cycle Al–OH species on the surface, which are responsible for the catalytic activity.

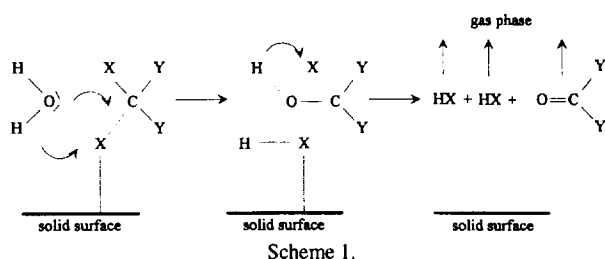
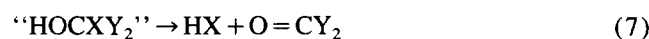
Furthermore, it should be stated that the theoretical content of fluorine in a pure AlF₃ phase would be 67.8% but in practice we found only 32.5% even after long reaction times. So in fact there is a remarkable content of oxidic phases, most probably covered by aluminium fluoride, but which are X-ray amorphous and can be disregarded for the catalytic process owing to the protecting AlF₃ layer. However, the experimental results clearly show stable long term activity of the fluorinated γ -alumina without any fundamental changes in the chemical composition and the reactivity still after 25 h.

4.2. Mechanism

Considering the very similar physical properties of HF and H₂O one could expect a similar mechanism for the heterogeneous catalyzed hydrolysis in comparison with the catalyzed chlorine–fluorine exchange, whereas in principle the first one can be regarded as an “extended” halogen exchange reaction. Although the following discussion remains to some extent speculative, it is based on the experimental results. In the first step one or both reactants will therefore be adsorbed onto the solid surface at suitable acidic centres, resulting in a reaction according to Eq. (5).



According to Scheme 1, in the first step an HX molecule will possibly split from the halomethane, producing an “in situ trihalogenomethanol” which itself is unstable and which will immediately stabilize under further HX-splitting, resulting in the formation of phosgene:



Additionally, the high amounts of HF formed as a result of hydrolysis would cause a very fast chlorine for fluorine exchange. Furthermore, the phosgene formed will immediately hydrolyze under these conditions (H₂O atmosphere), forming CO₂ and HY:



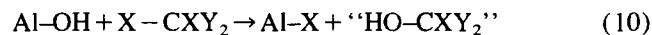
So finally, this reaction scheme represents Eq. (3). It is unclear which halogen bond will be hydrolyzed first, whether the C–Cl or the C–F bond represented by C–X in the scheme. However, the HF (or COF₂) formed under these conditions will undergo further reactions with the alumina as discussed above.

Another cycle could consist of two heterogeneous reaction steps, which can be considered as consecutive reactions where the solid phase is directly included in the reaction. The following considerations assume that the solid surface has been halogenated already as a result of the conditioning process.

In this case water should be able to partly hydrolyze the surface Al–X bonds, forming Al–OH bonds according to Eq. (9) (Brønsted sites). This reaction can be considered to be a dynamic equilibrium.



However, the halomethane molecule can now react directly with a surface hydroxyl group (Eq. (10))



As discussed above, the trihalogenomethanol is unstable and decomposes immediately according to Eq. (7) and Eq. (8), respectively.

The back reaction according to Eq. (9) is in fact a halogenation reaction of the solid surface. In principle, in addition to the hydrogen halides HF and HCl some other halogeno-compounds, e.g. COF₂, COCl₂ or COClF, can act as halogenating agents too. From the thermodynamic point of view (Table 1), the reaction of HCl is less probable and also the phosgenes should undergo hydrolysis reactions under these conditions. Finally, only the reaction with HF has to be considered as a consecutive reaction for the direct heterogeneous reaction of the halomethane with a surface hydroxyl group.

As can be seen from Fig. 2(a), owing to the hydrolysis reactions, CClF₃ is formed in considerable amounts. If the destruction of CCl₂F₂ alone occurred according to the second reaction pathway (direct solid/gas reaction), CClF₃ could never be formed. The question is, how is the higher fluorinated halomethane formed? There are at least two different mechanisms which have to be considered:

(i) Dismutation reactions of CCl₂F₂ occur, catalyzed by the fluorinated γ -alumina, which is principally known from literature [15,16]. In this case all representatives of the CCl_{4-n}F_n series should appear in the product mixture. However, only CClF₃ as a major component and lesser amounts of incompletely reacted CCl₂F₂ can be detected. The disappearance of CF₄ (we consistently found only traces of it) is

owing to the fact that CClF_3 is very stable (see free reaction enthalpies in Table 1) and does not undergo any remarkable dismutation reactions [15]. Otherwise, there are thermodynamic and kinetic reasons for the disappearance of CCl_3F and CCl_4 in particular. From the thermodynamic point of view the hydrolysis of higher chlorinated compounds is more supported than that of higher fluorinated ones (Table 1). In the same way higher fluorinated compounds are kinetically more resistant [15,16]. Consequently, the dismutation reaction of a CCl_2F_2 molecule can be considered as a precondition for the formation of less stable halomethanes (CFC-10 and CFC-11) which can easily hydrolyze under these conditions. As a result we checked the catalyzed hydrolysis of CCl_4 and CClF_3 . We found that even at 673 K a complete conversion of CCl_4 to CO_2 can be obtained, thus explaining the disappearance of CCl_4 and CCl_3F in the reaction system $\text{CCl}_2\text{F}_2/\text{H}_2\text{O}/\text{catalyst}$. On the contrary, CClF_3 hydrolyzes at temperatures of 773 K only to a very small extent. For a dismutation reaction according Eq. (1) the dismutation ratio (DR) would be at least

$$\text{DR} = \frac{n_{\text{CFC}-13}}{n_{\text{CFC}-11} + n_{\text{CFC}-10}} = 1/3$$

However, in case of complete dismutation reactions of CCl_2F_2 the conversion should be at least in the range of 25%! Only if the dismutation reactions of CCl_2F_2 are less and if the CFC-12 itself undergoes hydrolysis reactions to a large extent, the experimentally observed, relatively high conversion degrees of CCl_2F_2 can be explained according to the dismutation mechanism.

In order to check if dismutation reactions really do occur, stable conditions of the hydrolysis reactions of CCl_2F_2 were established, as already presented in Fig. 2(a), after 270 min. After this time the water flow was stopped and the gas phase compositions were monitored as a function of the reaction time. Immediately a continuous increase in all dismutation products with the reaction time occurs owing to the replacement of surface OH-groups by halogen according to Eq. (9) (back reaction) or (10), resulting in a dismutation activity of the catalyst surface. After an additional supply of water the catalytic hydrolysis reactions become dominant again, leading to the same product distribution as before.

A further reaction was performed using a pulse technique. Because a pulse technique, which we have already described and which we have used successfully for isomerization reactions of HFC-134 [17], allows a very sensitive detection of the changes occurring at the catalyst surface, the reversibility of the halogenation–hydrolysis reaction of the catalyst surface was repeated employing this technique. The apparatus used has already been described elsewhere. Here, 600 mg of the catalyst was placed into a flow reactor through which was passed a continuous carrier gas stream of nitrogen. Single pulses of the gaseous reactant were given to this stream in volumes of 1 ml. The hydrolysis reaction was carried out up to the same point as described above (stable hydrolysis reac-

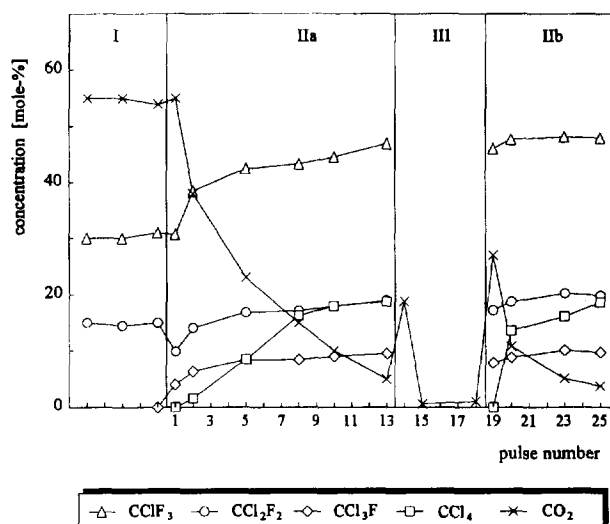


Fig. 5. Changes of the product distributions depending on the experimental conditions used: I, $\text{CCl}_2\text{F}_{2(\text{g})}$ and $\text{H}_2\text{O}_{(\text{g})}$ (hydrolysis); IIa, only $\text{CCl}_2\text{F}_{2(\text{g})}$ (dismutation); III, only $\text{H}_2\text{O}_{(\text{g})}$ (desorption of halomethanes); IIb, only $\text{CCl}_2\text{F}_{2(\text{g})}$ (dismutation).

tions comparable to the point at 270 min in Fig. 2(a)). Then the water supply was stopped again, so that the curves in Fig. 5 start with the first pulse of CCl_2F_2 (without water). Even the first experimental point clearly indicates the initial changes. There is a continuous increase in the formation of the dismutation products but in addition to that there is always a decreasing but not disappearing content of CO_2 which is obviously owing to reactions according to Eq. (10). Then the CCl_2F_2 supply was stopped (first vertical line between the 14th and 15th pulse in Fig. 5) and water pulses were given instead. Only with the first pulse of water do extreme changes of the product distribution occur. The fluorinated halomethanes completely disappear and after the following pulses only small amounts of CO_2 were detectable.

The second vertical line (between the 18th and 19th pulses) defines again the switch from water to CCl_2F_2 pulses. Immediately, the dismutation reactions become dominant again. Of note is the disappearance of CCl_4 after the first pulse, accompanied by a comparatively high content of CO_2 . This can obviously be regarded as a result of the preferable hydrolysis reactions of CCl_4 with adsorbed water according to Eq. (5) or with surface-OH-groups according to Eq. (10).

(ii) Hydrofluorination reactions of CCl_2F_2 with HF according to Eq. (11) could be an alternative reaction pathway in order to explain the formation of stable CClF_3 .



As a result of the hydrolysis reactions enormous amounts of HF are formed, providing the opportunity for hydrofluorination reactions. These reactions are well known and have been used for a long time for the production of CFCs. Consequently, this reaction pathway could explain the formation of CClF_3 which is stable under these conditions, whereas all the higher chlorinated methane derivatives are less stable and hydrolyze.

We checked a chromia catalyst in the same manner. A chromia surface becomes fluorinated more quickly than alumina, as has been shown previously [20]. X-ray analysis revealed mainly α -CrF₃ as the solid product in the surface. In contrast to the alumina system, the fluorination reactions of the solid are hindered by the formation of a solid protecting fluoride layer. Consequently, the uptake of HF formed during the hydrolysis reaction is less, this being the reason for a shorter conditioning period. Moreover, the hydrolyzability of a Cr–F bond is easier, which explains the slightly increased conversion degrees in comparison with γ -alumina.

5. Conclusions

A clear discrimination between the dismutation or hydrofluorination mechanism is not possible. It seems to be proved that both reactions occur in this complex reaction system but that hydrofluorination has a higher impact to the formation of CFC-13. There is no doubt that the higher fluorinated halomethanes are more stable than the less-fluorinated ones and cannot be destroyed under these conditions.

From the present results a suitable catalyst for hydrolysis reactions of halocarbons should provide the following general properties:

- The catalyst should be very active for the hydrolysis reactions of the haloalkane.
- The catalyst should not catalyze dismutation reactions. If dismutation reactions occur, higher fluorinated haloalkanes will be formed which cannot be destroyed as easily as less-fluorinated ones. Since dismutation reactions are preferably catalyzed by certain metal fluorides, those metal oxides have to be selected which form metal halides with at least partial hydrolyzability in order to depress dismutation reactions.
- The catalyst should not catalyze hydrofluorination reactions in order to prevent the formation of stable higher fluorinated halocarbons. Again, these reactions are pref-

erentially catalyzed by metal fluorides. Consequently, the same conditions apply for the catalyst as discussed before.

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