Journal of Thermal Analysis and Calorimetry, Vol. 72 (2003) 75–82

HYDRODECHLORINATION OF CF_3–CCl_2F (CFC-114a) ON Pd/β-AlF_3

An application of PulseTA®

M. Feist[*], *I. K. Murwani and E. Kemnitz*

Institute of Chemistry, Humboldt University, Brook-Taylor-Str. 2, 12489 Berlin, Germany

Abstract

The formation of CF_3–CH_2F (HFC-134a) by catalytic hydrodechlorination of CF_3–CCl_2F (CFC-114a) has been studied utilizing the recent PulseTA® technique. Instead of hydrogen as reactant, deuterium was used which facilitates the detection of the reaction products, i.e. the discrimination of various hydrofluorocarbons (HFC), by mass spectrometry. The product composition confirms a reaction mechanism via the carbene CF_3–CF. Water traces which are retained in the channel structure of the catalyst interact with chemisorbed deuterium thus explaining the formation of hydrogenated fluorocarbons as well. The obtained results demonstrate the potential of the pulse technique for the investigation of solid state reactions.

Keywords: fluorocarbons, hydrodechlorination, hydrofluorocarbons, pulse thermal analysis

Introduction

It is widely recognized that the catalytic conversion of unwanted chlorofluorocarbons (CFC) into CFC-alternatives can be a more attractive option for its disposal than by combustion. Hydrogen containing CFC-alternatives (HFC's) are especially promising taking into account their considerable lower hazard potential towards the ozone layer deplition. Our interest was dedicated to possible routes on a laboratory scale for the conversion of CFC's in heterogeneously catalysed processes which do not require the use of anhydrous hydrogen fluoride [1]. We studied the catalytic properties of various crystalline modifications of AlF_3 with respect to this type of halogen exchange reactions between 200 and 400°C. The experimental results obtained by applying various instrumental methods including GC, XRD, BET, XPS, XANES have been reviewed recently [2].

In the present study, we applied the PulseTA® technique to the investigation of a hydrodehalogenation reaction with palladium-supported β-AlF_3 as a catalyst. Pd/β-AlF_3 adopting the hexagonal tungsten bronze structure [3] revealed to be especially interesting in catalysis which is related to its channel structure together with the strong Lewis acid surface sites [4]. PulseTA® had been developed by Maciejewski *et al.* as an extension of

---

[*] Author for correspondence: E-mail: feistm@chemie.hu.berlin.de

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

the hyphenated techniques in thermal analysis (TA-MS, TA-FTIR) and is applicable to various capillary or skimmer coupled TA equipment [5]. It is normally utilized for the quantitative interpretation of the spectrometric signals obtained in coupled TA-MS or TA-FTIR systems and is based on a preceding calibration of the ion current (IC) or IR signals. This calibration can be performed on line by injecting permanent gases or liquids into the purge gas stream or off line by a preceding separate TA run of a suitable calibration substance.

In the present case, the TA apparatus has been utilized in terms of a catalytic reactor equipped with the PulseTA® device allowing for the injection of one or two permanent gases onto a sample subjected to a controlled heating program. Therefore, the chemical information about the gas composition obtainable via the IC curves of appropriate mass numbers is completed by TG data. As a consequence, also chemisorption and/or physisorption phenomena of the catalyst can be followed.

Experimental

The preparation of the catalyst started with basic aluminium acetate which was dissolved in 40% HF in order to precipitate α-$AlF_3 \cdot 3H_2O$. The trihydrate was then thermally decomposed yielding β-AlF_3 if the temperature does not exceed 280°C. In order to avoid pyrohydrolysis, the special reaction conditions of a self-generated atmosphere were applied [6]. Subsequently, β-AlF_3 was impregnated with a solution of $PdCl_2$ then dried in air at 120°C. The catalyst was activated by reduction. In order to obtain hydrogen-free catalysts, aqueous hydrazine was chosen as reducing agent. Excess hydrazine was removed by drying at 130°C for 12 h. A dark grey powder of Pd (7.5%)/β-AlF_3 was obtained.

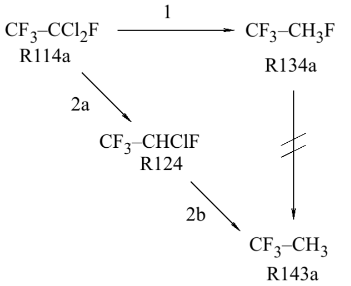
A NETZSCH thermoanalyzer STA 409 C Skimmer® system equipped with a quadrupole mass spectrometer BALZERS QMG 421 was used for recording the thermoanalytical curves (T, TG, DTG) together with the ionic current (IC) curves in the multiple ion detection (MID) mode [7]. A TG sample carrier system with corundum plate crucibles (17 mm diameter) and Pt/PtRh10 thermocouples was used. A constant purge gas flow of 70 mL min^{-1} N_2 (MESSER-GRIESHEIM 5.0) and a constant heating rate of 10 K min^{-1} were applied to samples of 12–29 mg. Injection gases were 1,1-dichloro-1,2,2,2-tetrafluoroethane (CFC-114a), 2-chloro-1,1,1-trifluoroethane (HFC-134a) both obtained from SOLVAY as well as deuterium (MESSER-GRIESHEIM 2.7).

The raw data have been evaluated utilizing the manufacturer's software PROTEUS v. 4.1+ and QUADSTAR 422 v. 6.02 without further data treatment, e.g. such as smoothing.

In order to minimize surfacial OH groups on the catalyst, a thermal pre-treatment preceded each measuring run. The samples were heated up to 280°C in nitrogen; typical mass losses amounted to 5–6%.

Results and discussion

Scheme 1 depicts the reaction system investigated in the present study. Two pincipal routes are possible when CFC-114a (CF_3–CCl_2F) reacts with hydrogen catalysed by Pd/β-AlF_3. The reaction (1) yields HFC-134a (CF_3–CH_2F) via the carbene CF_3–CF: whereas reactions (2a) and (2b) represent the stepwise hydrodehalogenation. Previous results indicated that the direct transformation of HFC-134a into HFC-143 as a consecutive reaction practically does not occur. Furthermore, the carbene formation mechanism was favoured [4]. This means that the discrimination between the two possible reaction routes is related to the discrimination between the various mentioned HFC's. Our aim was to apply the PulseTA® technique to that problem in order to contribute to an explanation of the reaction pathway. Appropriate mass numbers were followed to prove the direct formation of HFC-134a and/or the conditions for the non-formation of HCFC-124. Instead of hydrogen, we injected deuterium as the second reactant. The background was to better distinguish between the products of the mentioned reaction pathes (i.e. DCl) and the product of the side reaction with the hydroxyl groups present on the catalyst surface (i.e. HCl). The presence of OH groups is inevitable which is explained by the preparation route. The thermal pretreatment only minimizes the number of active OH groups.



Scheme 1

In the given system, only very few mass numbers allow for an unequivocal decision about the presence or absence of a CFC in the gas phase. This is true for the mass numbers *m/z* 33 (CH_2F^+) and *m/z* 34 ($CHDF^+$) indicating HFC-134a, *m/z* 65 (CH_3–CF_2^+) for HFC-143a, as well as *m/z* 21 (DF^+) and *m/z* 39 ($D^{37}Cl^+$). All other mass numbers can represent more than one compound and, hence, can be interpreted only regarding the relative changes of the IC intensities which can be expressed more or less intensively. Table 1 regroups extracts from the NIST library spectra of the hydrogenated CFC's together with the corresponding mass numbers of the deuterated compounds. The framed mass numbers permit to distinguish one CFC from each other.

Table 1 Mass numbers *m*/*z* (Intensity in %) for the detection of CFC's (extracted from the NIST library spectra with characteristic differences framed)

CF_3–CCl_2F CFC-114a	CF_3–CHClF HCFC-124	CF_3–CH_2F HFC-134a	CF_3–CH_3 HFC-143a	Fragments
31 (52)	31 (49)	31 (18)	31 (12)	CF^+
–	–	33 (100)	33 (8)	CH_2F^+
–	–	34 (100)	34 (8)	$CHDF^+$
35 (18)	35 (8)	35 (100)	35 (8)	CD_2F^+, $^{35}Cl^+$
–	51(52)	51 (20)	51 (3)	CHF_2^+
–	52 (52)	52 (20)	–	CDF_2^+
–	–	–	65 (40)	$CH_3-CF_2^+$
66 (18)	–	–	66 (1)	$C^{35}ClF^+$
–	67 (100)	–	67 (40)	$CHClF^+$, $CHD_2-CF_2^+$
68 (8)	68 (100)	–	–	$CDClF^+$, $C^{37}ClF^+$
69 (40)	69 (27)	69 (72)	69 (100)	CF_3^+
82 (5)	82 (5)	82 (5)	82 (1)	CF_3CH^+, $C^{35}Cl_2^+$
–	–	83 (65)	83 (2)	$CF_3CH_2^+$
84 (5)	84 (5)	84 (65)	84 (1)	CF_3CHD^+, $C^{35}Cl^{37}Cl^+$
85 (57)	85 (1)	85 (65)	–	$CF_3CD_2^+$, $CClF_2^+$
101 (80)	101 (40)	101 (1)	–	CCl_2F^+, CF_3CHF^+
–	102 (40)	102 (1)	–	CF_3CDF^+, $CF_3CH_2F^+$
135 (100)	–	–	–	CF_3CClF^+

Formation of HFC-134a

A comparison of Figs 1 and 2 clearly proves the formation of HFC-134a which can be followed via the signal of *m*/*z* 34 ($CHDF^+$). It is already detected at about 100°C (Fig. 2) whereas it does not occur at all if deuterium is absent (Fig. 1). The second product, DCl, is unequivocally indicated by the very characteristic signal of *m*/*z* 39 ($D^{37}Cl^+$).

The TG curve in Fig. 1 does not show any adsorption. The pulses of CFC with higher density cause only temporary buoyancy changes. The constant signal intensity of the IC curve** for *m*/*z* 101 shows that no educt consumption occurs. If deuterium is pulsed simultaneously, however, the first pulse effects chemisorption of D_2 on the catalyst whereas the further pulses only give the buoyancy effect. Consequently, the integral IC intensity of the first pulse is lower than for the following one. The decrease in IC intensity for the last pulses is due to the consumption of CFC-114a by the hydrodechlorination reaction and corresponds to the increasing intensity of the product peaks, e.g. *m*/*z* 34, indicating the formation of HFC-134a.

** Note that the signal intensity is given not by the peak height but by the integral intensity (in *A*·*s*).

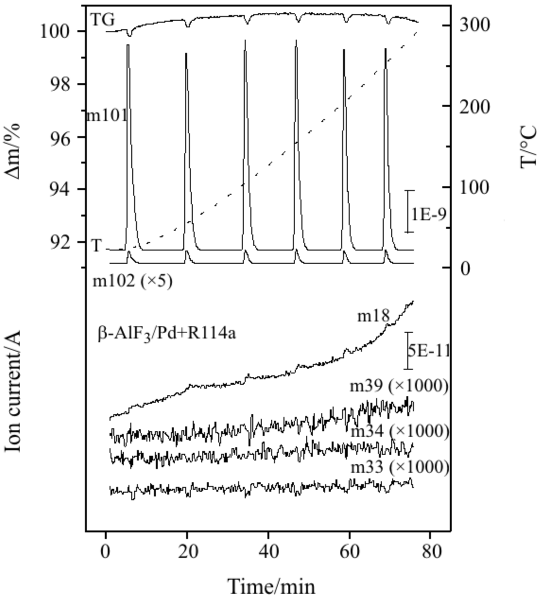


Fig. 1 500 μL pulses of CFC-114a onto Pd/β-AlF_3 without D_2 for increasing temperature. The *m*/*z* 101 (CCl_2F^+) represents the injected CFC-114a. Excepted the buoyancy change due to the CFC pulse, no interaction with the catalyst occurs

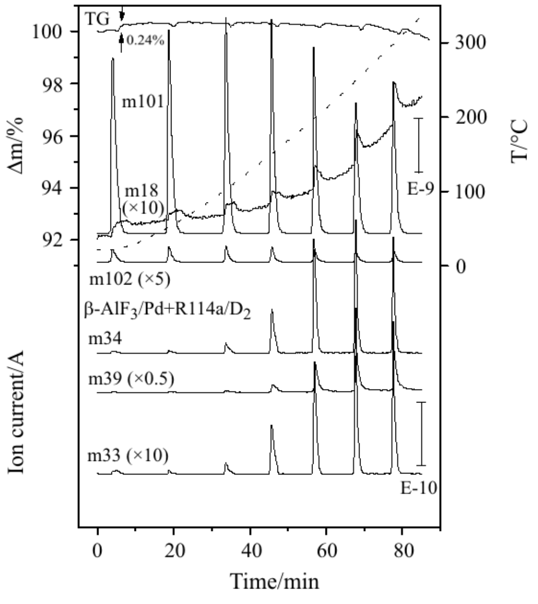


Fig. 2 500 μL pulses of CFC-114a onto Pd/β-AlF_3 with simultaneous pulses of 500 μL D_2 for increasing temperature. Note the mass gain for the first pulse which is due to chemisorption of D_2 on the metal sites on the catalyst surface

Discrimination between HCFC-124 and HFC-134a (Non-formation of HCFC-124)

Due to the characteristic mass numbers, a discrimination between HCFC-124 and HFC-134a is already possible by proving unequivocally the presence of HFC-134a (cf. Table 1). On the other hand, this can be additionally supported by the following considerations.

A comparison of the IC curves for *m/z* 52 and 102

The *m/z* 52 (CDF_2^+) which belongs to the spectra both of deuterated HCFC-124 and HFC-134a is formed in the MS by rearrangement. A decision to which compound it has to be attributed can be made by regarding the *m/z* 102. If the *m/z* 102 (CF_3–CDF^+) remains unchanged and low as shown in Figs 1 and 2, it does not represent HCFC-124 the mass spectrum of which comprises *m/z* 102 as an important mass number (40%, cf. Table 1). Consequently, also *m/z* 52 does not belong to HCFC-124 but to HFC-134a. Only a significant increase of the intensity of *m/z* 102 (CF_3–CDF^+) would indicate the formation of HCFC-124 but this is not observed.

The IC curve for *m/z* 68

The analysis of isotopic peaks is especially complicated but in the context of the discussion above the following considerations are helpful. The great intensity difference between the isotopic peak *m/z* 68 ($C^{37}ClF^+$) of the educt CFC-114a and the base peak ($CDClF^+$) of the deuterated HCFC-124 should enable us to discriminate between both CFC's (cf. Table 1). Figure 3 demonstrates that practically no intensity change occurs. This means that the *m/z* 68 represents the educt only thus confirming the non-formation of HCFC-124. Furthermore, the IC intensities for *m/z* 68 and *m/z* 52 change differently with increasing temperature which indicates that they do not originate from the same molecule. This also proves that *m/z* 52 belongs to HFC-134a whereas the non-changing *m/z* 68 does not represent HCFC-124 but the educt.

Injection of the intermediate HFC-134a

As shown before, the direct formation of HFC-134a and of DCl together with the non-formation of HCFC-124 could be proved unequivocally. This strongly supports the carbene formation mechanism. As mentioned earlier, the next hydrodehalogenation step, i.e. the formation of HFC-143a, practically does not occur which is due to the low stability of the corresponding carbene intermediate. Note that in this case not DCl but DF would be the hydrodehalogenation product. In order to prove directly the non-formation of HFC-143a, we injected HFC-134a, which has been shown to be the product of the first reaction stage, onto the catalyst and checked for the formation of DF. Figure 4 shows that no intensity increase for *m/z* 21 (DF^+) occurs which proves the non-formation of deuterated HFC-143a and DF as well. Also the hydrogenated HFC-143a is not formed as can be seen by the lack of intensity changes for *m/z* 65 (CH_3–CF_2^+) (see below).

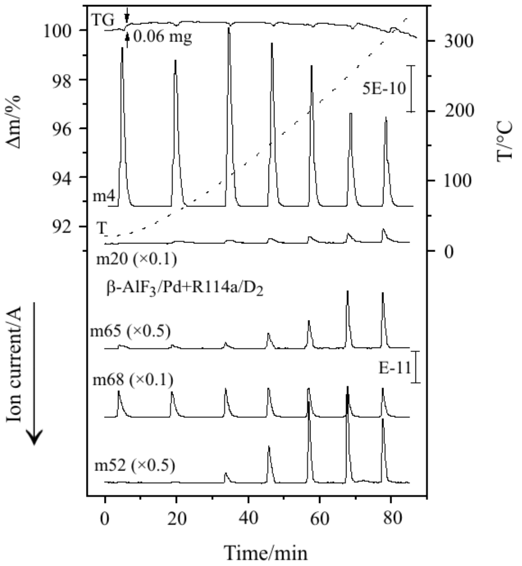


Fig. 3 500 μL pulses of CFC-114a onto Pd/β-AlF_3 with simultaneous pulses of 500 μL D_2 for increasing temperature. Additionally to Fig. 2, the following details on the reaction behaviour can be deduced: a – the consumption of the second educt via the m/z 4 (D_2^+), b – the formation of hydrogenated species (see text) evidenced by the m/z 65 ($CH_3{-}CF_2^+$) and c – the formation of the by-product HF (m/z 20) at higher temperatures

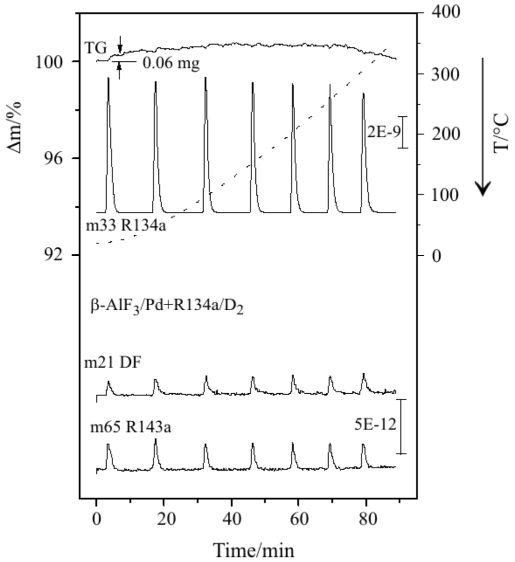


Fig. 4 500 μL pulses of CFC-134a (!) onto Pd/β-AlF_3 with simultaneous pulses of 500 μL D_2 for increasing temperature. Note that when injecting CFC-134a, not DCl but DF would be the product of the hypothetical last hydrodehalogenation step

Formation of hydrogenated species

On the other hand, the IC curve for *m*/*z* 65 (CH_3–CF_2^+) in Fig. 3 shows that a certain amount of HFC-143a is formed when the main hydrodehalogention reaction takes place. As the educt CFC-114a does not contain hydrogen, the single explanation of this unexpected finding is the interaction of the activated D^* species with traces of water in the channels of the HTB structure of Pd/β-AlF_3. It had been shown elsewhere that a residual amount of the small molecules hosted in the channels (i.e. water, ammonia, etc.) necessarily acts as stabilizing factor for the HTB structure and that the structure collapses when the molecules are totally removed [8]. This means that, in spite of the thermal pretreatment, hydrogen sources remain available in the reaction system, and several side reactions become possible via H-D exchange thus explaining the formation of hydrogenated species such as HFC-143a. In other words, we are reaching the limits of the applicability of the given catalyst system.

Conclusions

The MS control of the product composition formed during simultaneous pulsing of CFC's and deuterium showed that not only the principal hydrodechlorination reaction occurs. In addition to the expected deuterated products indicating various stages of the CFC conversion, also interaction with residual water in the channels of the catalyst takes place. This leads to the detection of practically the whole spectrum of hydrogenated species which do not represent the main reaction of originally interest. The obtained results do not prove directly but agree with the carbene mechanism of the CFC conversion reactions which had been proposed earlier. The high catalytic potential of the HTB structure additionally being promoted by the metal supporting remains unequivocal as it is proved by good selectivity and high conversion rates for the HFC's. Finally, the PulseTA® technique revealed once again its high potential for the investigation of solid state reactions.

* * *

The helpful discussion of the results of M. Maciejewski (ETH Zürich) is gratefully acknowledged.

References

1 H. Bozorgzadeh, E. Kemnitz, M. Nickkho-Amiry, T. Skapin and J. M. Winfield, J. Fluorine Chem., 107 (2001) 45; 110 (2001) 181.

2 E. Kemnitz and J. M. Winfield, in Advanced Inorganic Fluorides, Eds T. Nakajima. B. Zemva and A. Tressaud, Elsevier, Lausanne 2000, Ch. 12, pp. 367–401.

3 A. Le Bail, C. Jacoboni, M. Leblanc, R. De Pape, H. Duroy and J. L. Fourquet, J. Solid State Chem., 77 (1988) 96.

4 E. Kemnitz et al., J. Fluorine Chem., in prepn.

5 M. Maciejewski, C. A. Müller, R. Tschan, W.-D. Emmerich and A. Baiker, Thermochim. Acta, 295 (1997) 167.

6 D.-H. Menz, J. Thermal Anal., 38 (1992) 321.

7 W.-D. Emmerich and E. Post, J. Thermal Anal., 49 (1997) 1007.

8 R. Hoppe and D. Kissel, J. Fluorine Chem., 24 (1984) 327.