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Interaction of trifluoromethane (CHF_3) with alkali hydroxides and carbonates

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ABSTRACT

Heterogeneous reactions of trifluoromethane (CHF_3) with solid alkali hydroxides and carbonates were investigated under static and dynamic conditions and at moderate temperatures. In all cases, main reaction is fluorination characterised by a complete decomposition (mineralisation) of the fluorinating agent, CHF_3, and the formation of solid metal fluorides, CO, and H_2O. Under specific conditions, CO and H_2O may react further through the water–gas shift reaction and form solid metal carbonate. Extent of fluorination strongly depends on temperature and is dictated by the nature of the solid precursor. Alkali hydroxides, KOH, NaOH, and LiOH, are the most reactive solids that start to react with CHF_3 at relatively low temperatures, 370–484 K. Onset temperatures for fluorination of corresponding carbonates are 100–150 K higher. Reactivity of the solids towards CHF_3 can be correlated with their basicity. Reactions are rationalised on the basis of an acid–base type of interactions between CHF_3 as a very weak C–H acid and the very strong basic oxygen species in the solids. These interactions apparently play a decisive role during the initial binding of CHF_3 molecule to the solid reactant, in this way enabling or facilitating other decomposition steps that finally lead to a complete destruction of the CHF_3 molecule. Total decomposition of CHF_3 with KOH or NaOH, achievable at relatively very low temperatures, could in some specific cases represent a possible alternative to the energy-demanding CHF_3 decomposition by incineration.

1. Introduction

Trifluoromethane (CHF_3, HFC-23) is a strong greenhouse gas with a very high global warming potential (GWP) of 14,800 kg CO_2 kg^{-1} [1]. Main source of CHF_3 is the production of chlorodifluoromethane ($CHClF_2$, HCFC-22) [2]. In the past, majority of the co-produced CHF_3 was released into the atmosphere, *i.e.* its global atmospheric abundance of 22.6 pmol mol^{-1} in 2009 was seven times higher than thirty years ago [3]. From the 1990s, a considerable reduction of CHF_3 emissions was achieved by a combination of two approaches: (i) thorough optimisation of the $CHClF_2$ production processes and (ii) thermal oxidation (incineration) of CHF_3 waste streams. Besides its beneficial environmental effects, incineration has some distinctive drawbacks: it is an energy intensive process that operates at about 1473 K, it consumes fossil fuels, and it converts a potentially useful fluorinated product (CHF_3) into metal fluorides, mainly NaF or CaF_2, that are usually disposed of as waste [4]. It is therefore not surprising that numerous studies related to CHF_3 include either its complete decomposition or conversion to more applicable fluorinated products.

CHF_3 is characterised by a remarkable thermal stability. Under homogeneous gas phase conditions, discernible thermal decomposition (pyrolysis) of CHF_3 to hydrogen fluoride, HF, and difluorocarbene, CF_2, starts above 973 K [5–7]. Majority of CHF_3 conversion processes was therefore studied at high temperatures, usually within the temperature range of 773–1273 K. Related homogeneous reactions of CHF_3 were, as a rule, rationalised on the basis of the initial thermally activated decomposition to CF_2 and HF [7–11]. On the other side, investigations of diverse heterogeneous reactions, either catalytic [10,12,13] or non-catalytic [11,14], demonstrated a strong influence of surface processes on initial CHF_3 decomposition and subsequent reactions. In the presence of sufficiently stable solid catalysts, some reactions with CHF_3 could be performed at temperatures that were noticeably lower than those required by the non-catalysed reactions [6,12].

Another class of heterogeneous reactions is characterised by a complete decomposition (mineralisation) of CHF_3. These reactions, usually performed at 573–973 K, include catalytic hydrolyses [15,16] and fluorinations with CHF_3 [17–22]. It should be noted that these processes operate at temperatures that are considerably lower than those used in the non-catalytic incineration. Fluorinations with CHF_3

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were occasionally used as alternative fluorination procedures for the conversion of a variety of metal oxides to the corresponding fluorides or oxyfluorides. Special attention was paid to the fluorination of γ-Al_2O_3 where bulk conversion to AlF_3 was achieved at 673–753 K [17,18]. In our previous studies, fluorination with CHF_3 at 573–753 K was used for the preparation of a number of partially or fully fluorinated Al_2O_3- [19–21] or Cr_2O_3-based [21,22] xerogels or aerogels for catalytic purposes.

All chemical reactions mentioned so far take place at relatively high temperatures that can be associated with the high energy required to activate the very stable CHF_3 molecule. Very little is known about the chemical behaviour of CHF_3 below the 573–673 K temperature range and there are apparently no reports about the interactions of CHF_3 with some reactive basic solids that might serve as possible low temperature mineralisers for CHF_3, like hydroxides or carbonates. In related reports, CHF_3 was found to be very resistant to hydrolysis in strong alkaline solutions, *e.g.* when contacted with concentrated $NaOD/D_2O$ solutions at 378 K it readily undergoes H/D isotope exchange that is however accompanied by an almost negligible extent of hydrolysis [23,24].

In the present study we investigated the interaction of CHF_3 with solid alkali hydroxides and carbonates, and some other salts at relatively mild conditions. Results are discussed on the basis of an acid–base type of interactions in which CHF_3 behaves as a very weak acid. This means that at low temperatures CHF_3 reacts through the direct interaction with the surface of the most active solids and not through the initial thermally induced decomposition to HF and CF_2, as postulated for the CHF_3 reactions taking place at high temperatures.

2. Experimental

Reagents and experimental techniques: All solid reactants were commercial chemicals of reagent purity; CHF_3, purity min. 98%, was purchased from Matheson Europe. All chemicals were used as received. CHF_3 was additionally checked by FTIR spectroscopy. Solids for all experiments were ground and sieved through a 1 mm sieve. All manipulations with solid reactants were performed in a glove box to avoid hydration and, in the case of hydroxides, also carbonate formation. Other halocarbons used in this study (trichlorofluoromethane, CCl_3F, dichlorodifluoromethane, CCl_2F_2, perfluoromethylcyclohexane, $C_6F_{11}CF_3$, chlorodifluoromethane, $CHClF_2$, and chloroform, $CHCl_3$, were also commercial chemicals of reagent purity, minimum 99%.

Deuterated sodium hydroxide (NaOD) was prepared by the reaction between metallic sodium (Aldrich) and deuterated water (purity 99.9% D_2O, Aldrich) in nitrogen atmosphere. Solution of NaOD was evaporated to dryness at 363 K. Solid product was afterwards dried at 673 K under dynamic vacuum for 20 h.

Batch reactor was a 100 ml vessel made of nickel. Before each experiment the reactor was washed with diluted nitric acid (~10%), deionised water and ethanol, and pumped out for 2 h. In a typical static experiment, solids were heated in the batch reactor filled with CHF_3 or other gaseous reactants for 20 h. Possible catalytic effects of the reactor material (nickel) on the methanation reaction (Eq. (6)) was verified by heating a mixture of CO and H_2, molar ratio of 2.5:1, at 623 K for 20 h in the nickel reactor normally used in batch experiments. Formation of CH_4 was confirmed by FTIR. In a replicated test performed in a glass reactor formation of CH_4 was not observed.

A plug flow reactor was made of a nickel tube with 5 mm i.d. The layer of the solid reactant was supported by a plug made of silver wool. The same flow reactor was used for temperature programmed experiments aimed to determine the fluorination onset temperatures for a series of alkali hydroxides and carbonates. Solids were pre-treated *in situ* at 573 K (hydroxides) and at 673 K (carbonates) in a flow of N_2. After cooling to room temperature, a constant flow of CHF_3, 9.1 vol.% in N_2, was applied and the temperature of the reactor was raised linearly with a heating rate of 1.8 K min^{-1}. Reactions in the plug flow reactor were monitored on-line by FTIR spectrometer, as described below.

Chemical analysis: Total fluorine contents were determined by direct potentiometry using fluoride ion-selective electrode following the total decomposition of solid samples in $NaKCO_3$ melts [25,26].

FTIR spectroscopy: FTIR spectra were recorded on Perkin Elmer Spectrum GX spectrometer with 2 cm^{-1} resolution. Spectra of the gaseous products from the batch reactor were recorded in an 8 mm gas cell equipped with KBr windows. Quantitative analysis of gaseous products was performed in the same cell after calibration with pure components, CHF_3, carbon monoxide, CO, and methane, CH_4, at different relative pressures. Intensities of lines at 2519 cm^{-1} for CHF_3, 2120 cm^{-1} for CO, and 2958 cm^{-1} for CH_4 were used for calibration.

The on-line IR-monitoring of the products from the plug flow reactor was carried out with a 10 cm gas flow cell made of polytetrafluoroethylene (PTFE) and equipped with NaCl windows. Spectra of the gaseous effluents were recorded continuously; usual scanning rate was 5 scans min^{-1}. Component-specific evolution profiles were constructed from the collected batch data using the capabilities of the Spectrum TimeBase (PerkinElmer) software. CO was found to be as a suitable marker for qualitative monitoring of CHF_3 reactions since it allows a clear and unhindered distinction from other components in the IR-spectra of bulk gaseous effluents. CO evolution profiles were constructed from the line at 2120 cm^{-1}. Fluorination onset temperatures were determined arbitrarily and correspond to the points where a clear shift from the background could be observed.

Powder X-ray diffraction (XRD): Powder diffractograms of solid products after fluorination were recorded on ItalStructures IPD 3000 diffractometer equipped with an image plate detector by using the Cu K_α radiation. Each sample was ground and filled in a 0.3 mm i.d. quartz capillary.

Mass spectrometry (MS): The products of some reactions were analysed by the low resolution 60° Nier Type Mass Spectrometer. The samples were introduced into the spectrometer through a 0.5 m long nickel capillary with 0.1 mm i.d. from a reservoir kept at 1.33 kPa. The samples were ionised by electrons at 35 eV and 10 μA trap current intensity. For ion detection an ETP electron multiplier (ATF151H) operating at 1.8 kV in analogue mode was used.

3. Results and discussion

3.1. Reactions under static conditions

Heterogeneous reactions between CHF_3 and different solid reactants under static isothermal conditions were studied in a batch reactor. Solid reactants, reaction conditions and compositions of the products are listed in Table 1. Majority of tests was performed with excess of CHF_3 to determine the fluorination end state achievable under the varying conditions. Extent of fluorination derived from the fluoride content of the solid products was used as a measure to compare the relative activities of various solids in the reaction with CHF_3.

Sodium hydroxide, NaOH, as the most common alkali hydroxide, was investigated in more details. Both temperature and the initial pressure of CHF_3 were varied to determine the influence of these two parameters on the CHF_3 decomposition reaction. Temperature was found to be a decisive factor in NaOH fluorination (tests NaOH-(1–7)). At temperatures up to 373 K the extent of fluorination was very low. In the temperature range

Table 1
Reaction conditions and composition of products for the interaction of CHF_3 with different solid reactants.

Solid reactant – Test No.	Temperature, K	Initial CHF_3 pressure, kPa	Molar ratio, CHF_3:solid	CO content in gas products, vol.%	F^- content in solid products, wt.%	Metal fluoride in solid products, wt.%
Hydroxides						
LiOH-1	523	357	1.00:1.90	56	37.9	51.8
NaOH-1	323	357	1.00:2.08	3.6	0.04	0.09
NaOH-2	373	357	1.00:2.23	11	0.1	0.2
NaOH-3	423	357	1.00:2.30	25	25.0	55.3
NaOH-4	473	357	1.00:2.24	38	29.6	65.4
NaOH-5	523	357	1.00:2.24	49	32.5	71.8
NaOH-6	573	357	1.00:2.24	62	39.7	87.7
NaOH-7	623	357	1.00:2.20	69	44.8	99.0
NaOH-8	523	357	1.00:10.8	0	11.6	25.6
NaOH-9	523	13	1.00:2.14	97	31.4	69.4
NaOH-10	523	67	1.00:2.81	59	29.6	65.4
NaOH-11	523	133	1.00:2.86	55	31.5	69.6
NaOH-12	523	266	1.00:2.90	50	30.8	68.1
NaOH-13	523	399	1.00:2.90	55	33.5	74.0
NaOD-1	523	237	1.00:1.81	44	32.1	71.0
KOH-1	523	357	1.00:2.10	37	30.5	93.3
$Ca(OH)_2$	523	357	1.00:0.92	60	27.7	56.9
Carbonates						
Li_2CO_3-1	523	357	1.00:1.15	2.3	0.09	0.12
Li_2CO_3-2	673	357	1.00:0.34	38	71.7	97.9
Na_2CO_3-1	523	357	1.00:0.89	2.9	0.23	0.51
K_2CO_3-1	523	357	1.00:1.03	2.4	0.3	0.9
$MgCO_3$	523	357	1.00:1.03	24	6.4	11.0
$CaCO_3$	523	357	1.00:1.00	13	2.1	4.3
$SrCO_3$	523	357	1.00:1.04	3.3	0.2	0.7
$BaCO_3$	523	357	1.00:1.03	40	6.3	29.0
Other salts						
Na_2SO_4	523	357	1.00:0.58	1.80	0	0
$Na_2C_2O_4$	523	357	1.00:1.04	3.10	0.02	0.04

373–423 K an abrupt onset of the reaction was observed, afterwards the extent of fluorination increased steadily with increasing temperature. The highest extent of fluorination, corresponding to an almost complete (99%) conversion to NaF, was achieved at the highest temperature investigated, 623 K (sample NaOH-7, Table 1). In contrast to temperature, fluorination was not significantly affected by pressure, at least within the pressure range investigated (tests NaOH-(9–13)). At the arbitrarily selected intermediate fluorination temperature of 523 K, conversion of alkali hydroxides to the corresponding fluorides was 51.8% for LiOH, 71.8% for NaOH and 93.3% for KOH, suggesting that the activity of alkali hydroxides towards CHF_3 varied in the order KOH > NaOH > LiOH. These findings correlate very well with the results of temperature programmed flow experiments (see Section 3.2). For the only alkaline earth hydroxide investigated within this study, $Ca(OH)_2$, conversion to fluoride was similar to that found for LiOH.

In contrast to hydroxides, alkali carbonates exhibited much lower activities towards CHF_3 at 523 K with typical conversions to fluorides that are almost two orders of magnitude lower as those obtained by the corresponding hydroxides (Table 1). Slightly higher conversions were obtained with some alkaline earth carbonates. As was the case with hydroxides, fluorination of carbonates was also strongly temperature dependent; for example, conversion of Li_2CO_3 to LiF increased from 0.12% at 523 K to 97.9% at 673 K (samples Li_2CO_3-1 and -2, Table 1). Other salts tested, sodium sulphate, Na_2SO_4, and sodium oxalate, $Na_2C_2O_4$, were found to be practically inactive towards CHF_3 at 523 K. Observed inactivity of $Na_2C_2O_4$ is in line with a previous study [27] where it was found that $Na_2C_2O_4$ reacts with perhalocarbons (CFCs) but not with partially halogenated compounds. It was suggested that in the reaction between CFCs and $Na_2C_2O_4$ the latter acts as a two-electron transfer agent to the fluorocarbon while the cation acts as an acceptor for the fluoride ion. On the other side, partially halogenated compounds are insufficiently powerful electron acceptors and do therefore not react with $Na_2C_2O_4$ [27].

Crystalline phases in samples after fluorination were determined by powder XRD. Diffractograms of some CHF_3-treated NaOH samples at different temperatures are shown in Fig. 1A. Products obtained at temperatures below 423 K consist of the unchanged NaOH phase what is in line with the very low fluoride content determined by chemical analyses (Table 1). Onset of fluorination at 423 K results in the formation of crystalline NaF. In the intermediate temperature region, 423–523 K, solid products are a mixture of NaF, minor quantities of sodium carbonate, Na_2CO_3, and non-reacted NaOH (Fig. 1A, samples NaOH-3 and -5). Na_2CO_3 is a side product formed from NaOH and CO_2, as described in Section 3.1.1. Gradual decrease of the Na_2CO_3 content above 523 K is the result of Na_2CO_3 fluorination. In addition, experiment performed with excess of NaOH, *i.e.* under limited fluorination conditions, demonstrated that a considerable amount of Na_2CO_3 was present also after treatment at 523 K (sample NaOH-8, Fig. 1C). XRD results of LiOH and KOH fluorination at 523 K are consistent with chemical analyses (Table 1) and indicate the formation of the corresponding well crystallised fluorides (samples LiOH and KOH, Fig. 1B). Contrarily, no crystalline fluoride phases were detected in CHF_3-treated carbonates (not shown) that can be associated with the relatively low extent of fluorination at 523 K (Table 1).

Reactive interaction of CHF_3 with solids containing oxygen results in the formation of solid fluorides and gaseous products, mainly H_2O and CO [17], and in the case of carbonates also CO_2. Amounts of CO formed in batch tests with different solid reactants and quantified by FTIR are summarised in Table 1. CO contents correlate well with the extents of fluorination of the solid phases and can be used as an additional indicator for the activity of the solids to decompose CHF_3. Exact quantification of the

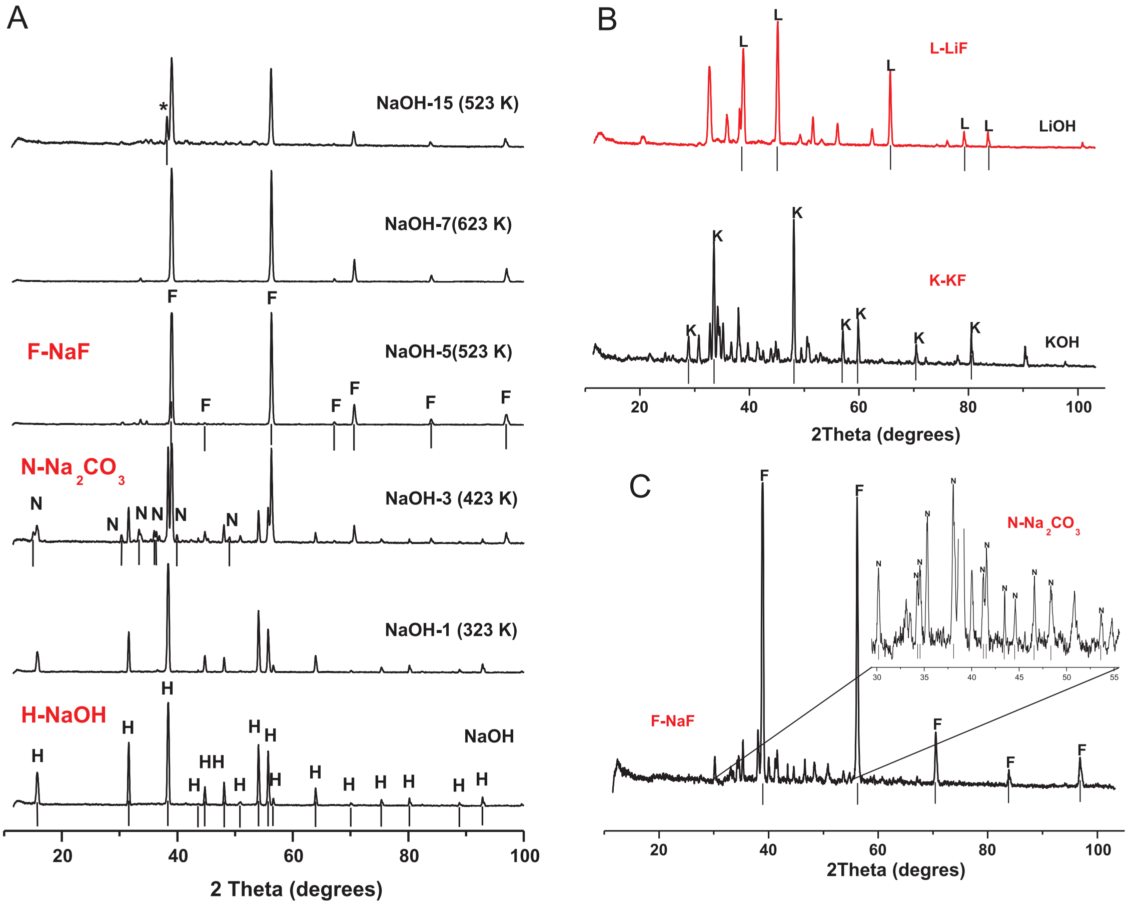


Fig. 1. Powder diffractograms of hydroxides after reaction with CHF_3: (A) NaOH fluorinated at different temperatures in the batch reactor (samples NaOH-1 to NaOH-7) and NaOH fluorinated at 523 K in the plug flow reactor (sample NaOH-15; * – Ag from silver wool plug); (B) LiOH and KOH fluorinated at 523 K in the batch reactor; (C) excess of NaOH fluorinated at 523 K in the batch reactor (sample NaOH-8).

fluorination processes in the batch reactor on the basis of CO data is however hampered by the occurrence of secondary reactions that may considerably alter the final CO contents (see Section 3.1.1 and Scheme 1).

In contrast to CO, formation of H_2O in the batch reactor could not be unequivocally determined by FTIR. Besides interferences with background H_2O and occurrence of side reactions, this can be the result of possible H_2O retention in the solid products, either by strong adsorption or by formation of various hydrated phases. To obtain a more definitive information about H_2O formation, NaOD was fluorinated with CHF_3 in a batch reactor at 523 K (sample NaOD, Table 1). Gaseous products of this reaction were analysed by MS. It should be pointed out that, even by using MS, H_2O or its deuterated analogues could not be unambiguously identified in the bulk gaseous products. Volatile products were therefore pumped off at room temperature and then the reactor was heated to 323 K. MS analysis of the headspace gases confirmed the presence of all three forms of water, H_2O, HDO and D_2O. These findings clearly demonstrate that H_2O is one of the main products in fluorinations with CHF_3 and that a considerable portion of the H_2O formed is strongly retained in the solid products.

Interaction of CHF_3 with alkali hydroxides or carbonates is therefore consistent with the following primary fluorination reactions (M = Li, Na or K):

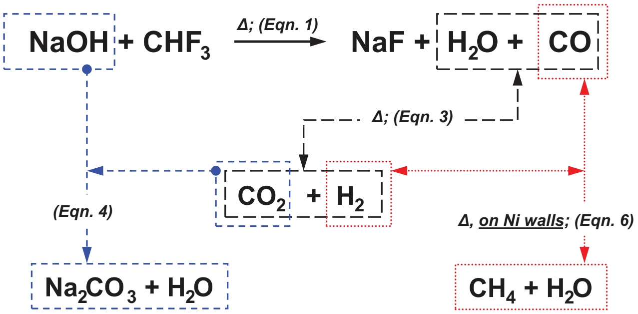
$$3MOH + CHF_3 \rightarrow 3MF + CO + 2H_2O \quad (1)$$

$$3M_2CO_3 + 2CHF_3 \rightarrow 6MF + 3CO_2 + 2CO + H_2O \quad (2)$$

3.1.1. *Side reactions with hydroxides*

Closer examination of the gaseous products from some batch tests revealed that in the interaction of CHF_3 with alkali hydroxides H_2 and CH_4 are also formed. Formation of these two gaseous products was especially noticeable at higher temperatures (Table 2). Main reaction between CHF_3 and NaOH and likely side reactions that take place in the batch reactor at intermediate temperatures are represented in Scheme 1.

Formation of H_2/CO_2 and alkali carbonate: Formation of H_2 was confirmed by MS in the products of some runs with NaOH or KOH



Scheme 1. Schematic representation of the main reaction between NaOH and CHF_3 (top line) and the possible side reactions leading to the formation of CO_2/H_2, Na_2CO_3 and CH_4 (marked with dashed/dotted lines). Scheme represents the likely situation in the temperature interval of 420–544 K; above 544 K Na_2CO_3 may react with CHF_3 (Eq. (2), not shown in the scheme). Exact stoichiometry of the indicated reactions is given in the text.

Table 2
Interaction of NaOH with CHF_3 in a batch reactor at different temperatures: composition of the gas phase determined by FTIR.

Name	Temperature, K	CO, vol.%	CHF_3, vol.%	CH_4, vol.%	H_2[a], vol.%
NaOH-1	323	3.6	96	0	0
NaOH-2	373	11	89	0	0
NaOH-3	423	25	75	0	0
NaOH-4	473	38	62	0	0
NaOH-5	523	49	51	0	0
NaOH-6	573	62	38	0.8	0
NaOH-7	623	69	17	1.2	13

[a] Determined from difference to 100%.

at 523 and 623 K (tests NaOH-5 and -7, and KOH, Table 1). In addition, H_2 and both of its deuterated analogues, HD and D_2, were detected by MS in the products of the reaction with NaOD at 523 K (test NaOD, Table 1). Very likely, H_2 is the product of the equilibrium water–gas shift reaction (Eq. (3)) between CO and H_2O; the latter two are products of the primary fluorination reaction (Eq. (1)).

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (3)$$

In the transitional stage of fluorination, equilibrium of reaction (3) is shifted to the right due to the reaction of CO_2 with the non-reacted hydroxide and the consequent formation of the solid carbonate (Eq. (4)). Formation of carbonate at intermediate temperatures was clearly confirmed by XRD measurements.

$$CO_2 + 2MOH \rightarrow M_2CO_3 + H_2O \quad (4)$$

In experiments with excess of CHF_3, evolution of H_2 from reaction (3) stops when all hydroxide is converted to fluoride or a mixture of fluoride and carbonate. This means that when the hydroxide is the limiting reactant only part of the CO formed in reaction (1) can react further. Analyses of the gaseous phases after reaction, presented in Tables 1 and 2, are consistent with this, indicating that, besides the non-reacted CHF_3, CO is the main gaseous product detected. On the other side, experiment with excess of NaOH (test NaOH-8, Table 1) demonstrated that under such conditions CO can be quantitatively converted to carbonate, as confirmed by XRD (Fig. 1C). In this specific case, *i.e.* excess of NaOH and long contact times, interaction between alkali hydroxides and CHF_3 can better be represented by the following overall equation:

$$5MOH + CHF_3 \rightarrow 3MF + M_2CO_3 + H_2 + 2H_2O \quad (5)$$

Formation of CH_4: Formation of CH_4 at levels detectable by FTIR was observed in some NaOH tests at higher temperatures (tests NaOH-6 and -7, Table 2). CH_4 is very likely formed by CO methanation (Eq. (6)) that is strongly catalysed by nickel or nickel-based materials at 523–673 K [28,29].

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad (6)$$

Our tests (see Section 2) confirmed that under the experimental conditions used within the current study, nickel from the reactor can act as an active methanation catalyst.

3.1.2. Reactions with other halocarbons

Activity of CHF_3 towards NaOH was compared with that exhibited by some representative halocarbons. Experiments with these compounds were performed in the batch reactor under conditions similar to those used in the CHF_3/NaOH investigations. Reaction conditions and the corresponding fluorine contents are presented in Table 3.

Results demonstrate that all investigated perhalogenated compounds, CCl_3F, CCl_2F_2, and $C_6F_{11}CF_3$, exhibit very low activities towards NaOH. In all cases, fluorine content in the NaOH treated at 523 K is below 1 wt.%. On the other side, partially halogenated hydrocarbons, $CHClF_2$, and $CHCl_3$ (latter not included in Table 3), exhibit much higher activities. Fluorine content of the $CHClF_2$-treated NaOH is comparable to that obtained with CHF_3. In the case of $CHCl_3$, almost complete chlorination of NaOH was achieved already at 323 K what is in line with the previously determined relative reactivities of haloforms in basic hydrolysis [30]. Results presented here clearly show that hydrogen-containing partially halogenated compounds (HFCs and HCFCs) are less stable and noticeably more active towards NaOH than the very stable fully halogenated compounds.

3.2. Reactions under flow conditions

Some of the tests in the batch reactor were complemented by investigations performed under flow conditions in a plug flow reactor with a fixed layer of the solid reactant. Representative data for a series of isothermal flow tests with NaOH are presented in Table 4. Although the whole duration of flow tests was 9–15 h, the on-line FTIR monitoring of CO evolution showed that the reaction was virtually completed within the first hour on-stream. Fluoride contents in the solid products obtained under flow conditions are similar to those obtained at same temperatures in the batch reactor (Table 1). This indicates that in the interaction of CHF_3 with NaOH temperature is the dominant factor that determines the extent of fluorination. Although the overall reaction times for the two regimes differ considerably, they appear to be less significant at least within the time scales used in both sets of experiments.

Table 3
Interaction of different halocarbons with NaOH in a batch reactor at 523 K (test duration 20 h).

Compound	Molar ratio, Comp.:NaOH	Initial pressure, kPa	F^- content in solid products, wt.%
CCl_3F	1.00:9.71	100	0.60
CCl_2F_2	1.00:2.49	200	0.93
$C_6F_{11}CF_3$	1.00:10.0	100	0.11
$CHClF_2$	1.00:2.21	200	27.1

Table 4
Interaction of CHF_3 with NaOH in the plug flow reactor (CHF_3 flow: 1 $cm^3\,min^{-1}$).

Test	NaOH, g	Temperature, K	Layer height, mm	Contact time, s	Overall test duration, h	F^- content in solid products, wt.%
NaOH-14	0.044	473	2	2.4	9	30.3
NaOH-15	0.048	523	2	2.4	15	28.0
NaOH-16	0.137	523	6	7.2	10	29.1
NaOH-17	0.307	523	16	18.8	10	31.3

Table 5
Temperature programmed flow tests with alkali hydroxides and carbonates performed from room temperature to the indicated upper temperature (heating rate: 1.8 K min^{-1}; CHF_3/N_2 flow 11.0 cm^3 min^{-1}; 9.1 vol.% CHF_3).

Test	Upper temperature, K	Layer height, mm	Start of CO evolution[a], K
LiOH-2	573	1	484
NaOH-18	573	5	420
KOH-2	384	1	370
Li_2CO_3-3	673	5	581
Na_2CO_3-2	673	5	544
K_2CO_3-2	673	5	522

[a] Temperature at which a clear shift from the background could be established.

XRD results are consistent with chemical analyses and indicate the formation of NaF as the main crystalline phase (sample NaOH-15, Fig. 1A). In contrast to batch tests, products obtained under flow conditions do not contain relevant levels of Na_2CO_3. FTIR analyses of the effluents from the flow reactor were consistent with the formation of CO and H_2O as the main gaseous products. For the reasons mentioned before, evolution of CO was used to conveniently monitor the progress of fluorination. In a separate series of temperature programmed experiments, evolution of CO proved to be particularly suitable to determine the onset of fluorination for different alkali hydroxides and carbonates. Relevant data for these experiments are summarised in Table 5, with the corresponding CO evolution profiles shown in Fig. 2. Results clearly show that KOH is the most active solid that starts to react approximately at 370 K. For the hydroxides, the starting temperature of fluorination is increasing in the order KOH < NaOH < LiOH (Fig. 2A). Same trend is also observed for the carbonate series, although the corresponding temperatures are 97–152 K higher (Fig. 2B). This confirms that the carbonates are less active than the hydroxides. Such behaviour can be correlated with lower basicity of carbonates in comparison to hydroxides. It should also be noted that the results of temperature programmed experiments for hydroxides correlate very well with the activities deduced from the experiments performed under static conditions in a batch reactor (see Section 3.1). On the other side, temperature programmed experiments show that for the investigated carbonates fluorination starts above the reference temperature used in comparative static experiments (523 K). This is in accordance with the low extent of fluorination obtained with carbonates in the batch reactor.

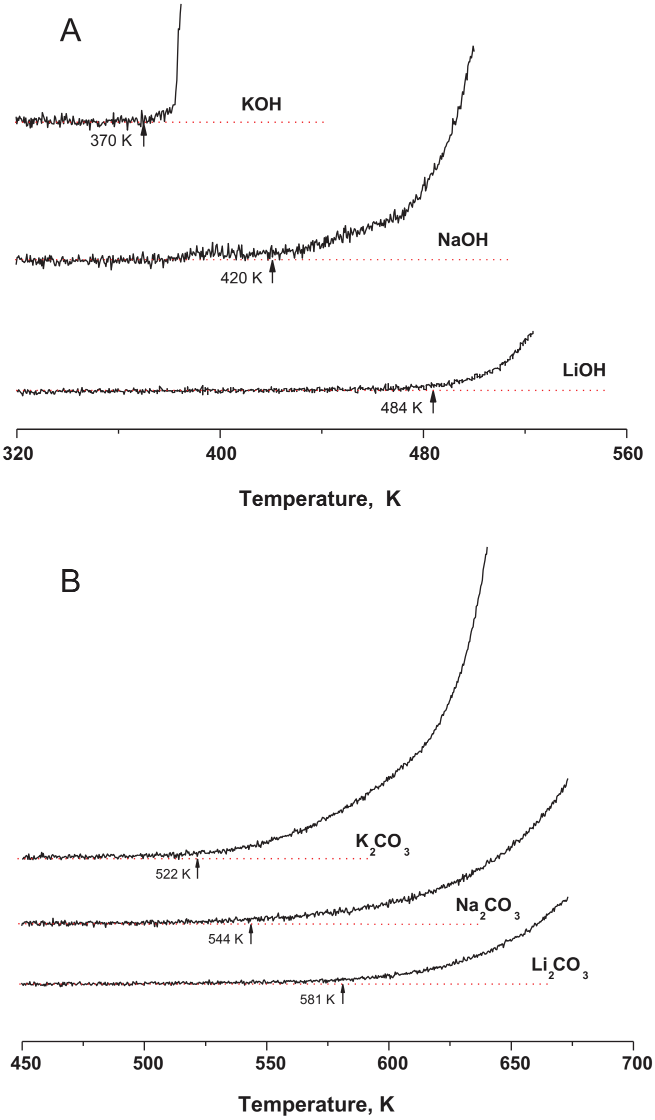


Fig. 2. CO-evolution profiles (offset) from temperature programmed experiments in a plug flow reactor: (A) reaction of CHF_3 with alkali hydroxides, (B) reaction of CHF_3 with alkali carbonates.

3.3. Comparison of CHF_3 reactions with hydroxides under static and dynamic conditions

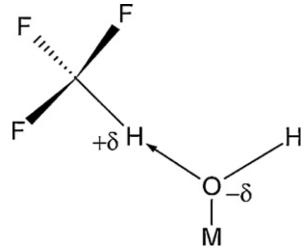
Interaction of CHF_3 with alkali hydroxides under static or dynamic (flow) conditions yields solid product with remarkably similar compositions. Under both reaction regimes, main reaction is fluorination and the hydroxide to fluoride conversion depends mainly on temperature. Similar conversions found under both reaction regimes indicate that hydroxide fluorination, although thermodynamically strongly favoured, is kinetically hindered probably by diffusion processes. Diffusion in gas-solid reactions depends strongly on the transport characteristics of the formed product layer. Since the molar volumes of alkali fluorides are smaller than those of hydroxides, non-compact fluoride layers are likely to be formed. Fluorination is therefore expected to proceed without significant diffusion control. However, reaction of CHF_3 with alkali hydroxides can be regarded as a classical gas–solid reaction only in the very initial stages when non-hydrated hydroxide is present. With the progress of reaction, hydroxide is hydrated by H_2O formed during fluorination (Eq. (1)). In the NaOH (or KOH)/H_2O systems melting temperatures are decreasing rapidly with increasing H_2O contents; *e.g.* respective hydroxide/hydroxide monohydrate melting points are 594/338 K for NaOH and 677/418 K for KOH [31]. This implies that under the reaction conditions used in the present study, evolution of H_2O could be accompanied by partial melting of the residual hydroxide phase resulting in a rather complex gas–(liquid)–solid reaction system. This aspect is of particular importance in batch experiments where the H_2O/unreacted hydroxide ratio is increasing rapidly with the advancement of fluorination. On the other side, physical state of the hydroxide phase has apparently no decisive effect on the fluorination process as a whole, as demonstrated by the batch experiment entirely conducted above the melting point of NaOH (test NaOH-7, Table 1). In the flow experiments, H_2O formed during fluorination is constantly removed from the reactor with the stream of effluents. H_2O levels within the reaction zone are therefore lower and more constant as in batch experiments. Occasional clogging of the flow reactor due the partial melting of the solid layer, observed mostly with KOH, indicated however that hydration may occur also under flow conditions. For these reasons, operation of the flow reactor with a fixed layer of solid reactant may become problematic already at temperatures that are considerably lower than the melting points of pure hydroxides. Pronounced susceptibility of KOH to melting can be associated with higher thermal stability of its hydrates in comparison with NaOH.

Experiments in the batch reactor with very long contact times allowed investigations at conditions that are closer to the equilibrium state. As mentioned in Section 3.1.1, this allowed a clear identification of the main side reactions that may take place in these reaction systems. Due to technical limitations, occurrence of side reactions under flow conditions could not be studied in detail. However, it can be assumed that due to much shorter contact times that do not allow adequate equilibration and lower concentrations of gaseous products, extent of side reactions in flow experiments is likely to be much lower as under static conditions. This assumption is partly supported by the absence of measurable amounts of carbonate in the solid and methane in the gaseous products from the flow reactions.

3.4. Activation of CHF_3 by hydroxides or carbonates through acid–base interactions

As mentioned in the introduction, a strong consensus exists that in homogeneous high temperature reactions CHF_3 is activated thermally through the pyrolytic decomposition to HF and CF_2. Same mechanism was also proposed for the fluorination of α-Al_2O_3 with CHF_3 above 1023 K. [11]. On the other side, CHF_3 activation mechanisms in heterogeneous reactions at temperatures below 973 K are much less clear and interpreted in a controversial manner. Some authors suggested that decomposition of CHF_3 on solid surfaces occurs by C–F bond activation through a $C–F\cdots M^+$ type of interactions [6,14,16]. Conversely, activity of CHF_3 in fluorination of γ-Al_2O_3 was interpreted by the initial rupture of the relatively weak C–H bond that leads to the formation of active fluorinating species [17]. These precedents, although somehow controversial, indicate that in heterogeneous reactions CHF_3 can be activated either thermally or chemically. Which of the two basic activation mechanisms prevails depends mainly on temperature and there is apparently a relatively narrow temperature limit between the two regions. Thermal activation with discernible CF_2 and HF formation is predominant above 973 K. Below this temperature and especially below 773 K, chemical activation through direct interactions of the CHF_3 molecule with the solid predominates.

As found in the present study, CHF_3 starts to react with alkali hydroxides and carbonates at 370–484 K and 522–581 K (Table 5), respectively. Fluorination onset temperatures for alkali hydroxides are, to the best of our knowledge, the lowest reported so far for bulk fluorination of solids with CHF_3. Alkali hydroxides show a remarkably higher activity towards CHF_3 than the corresponding carbonates. Reactivity of the latter is comparable or somewhat higher as that observed for some metal oxides that were usually fluorinated above 573 K. As indicated above, relatively very low reaction temperatures found in the present study indicate that activation of CHF_3 is very likely chemical, although the underlying surface processes leading to CHF_3 decomposition are not entirely understood. Mechanisms that include C–F bond activation seem however less probable since they do not account for large difference in activities towards hydroxides between HFCs and HCFCs, and fully halogenated fluorocarbons that were observed within this study (Section 3.1.2). Similar behaviour of these two groups of compounds was also observed in TPD experiments with partially fluorinated γ-Al_2O_3 [18], where it was pointed out that some interaction with the solid *via* hydrogen in HFCs/HCFCs must occur, but no other details about the nature of the presumed interactions were given [18]. It is therefore reasonable to propose that in the initial stage CHF_3, as a very weak C–H acid with estimated pK_a of 26–28 [23 and related references therein], interacts with very strong basic sites on the surface of the solids. In case of hydroxides and carbonates, basic sites correspond to oxygen atoms in hydroxide and carbonate ions. Possible acid–base interaction between CHF_3 and an alkali hydroxide is presented in Scheme 2.



Scheme 2. Possible acid–base interaction between CHF_3 and an alkali hydroxide.

Since the basicity of the oxygen in hydroxide ions is higher than in carbonate ions, interaction of CHF_3 with hydroxides will be stronger than with carbonates resulting in a higher activity of the former compounds. This correlates very well with current experimental findings. However, it should be noted that the proposed acid–base interaction of the type, $C–H\cdots O–M^+$, is only one of the steps, although apparently an important one, in the process of complete CHF_3 decomposition. Other steps very probably include also interactions of the type, $C–F\cdots M^+$, as intermediate stages in metal fluoride formation and in the decomposition of CF_x species that could also be formed as intermediates. Namely, FTIR investigations of CHF_3 adsorption on magnesia and alkali-exchanged Y-zeolites revealed that in the most probable adsorption complex CHF_3 binds to the solid simultaneously through $C–H\cdots O$ and $C–F\cdots M^+$ interactions, with the latter being much stronger due to the small size and high electronegativity of the fluorine [32,33]. It can be concluded that similar interactions are possible also in our systems although it is very likely that the relative strengths of the two interactions differ from those in oxide materials mentioned above. Namely, alkali cations in alkali oxides and related compounds exhibit very weak Lewis acidity [34] that probably results in much weaker $C–F\cdots M^+$ interactions.

4. Conclusions

Metal hydroxides and carbonates investigated in the present study react with CHF_3 at moderate temperatures (below 573 K). Basic reaction can be described as fluorination in which CHF_3 acts as a fluorinating agent. In this reaction, CHF_3 undergoes complete decomposition (mineralisation) with the formation of solid metal fluorides, and gaseous CO and H_2O. Under specific conditions, *i.e.* excess of hydroxide and sufficiently long contact times, water–gas shift reaction is an important side process in which CO is firstly converted to CO_2, and finally to solid metal carbonate. In this case, fluorine and carbon from CHF_3 are mineralised in the form of metal fluorides and carbonates.

Results obtained so far strongly suggest that basicity of the solids is the key factor that determines their reactivity towards CHF_3. Alkali hydroxides, the most reactive solids within this study, start to react with CHF_3 at temperatures that are 100–150 K lower than those determined for their carbonate counterparts. Reactions of CHF_3 with reactive solids are therefore rationalised on the basis of acid–base interactions between the acidic hydrogen in CHF_3 and the basic oxygen species in the solids. Although the exact CHF_3 decomposition mechanisms remain unclear, it is reasonable to conclude that the acid–base interactions play an important role in the initial binding of CHF_3 molecule to the solid reactant. In this way they enable or facilitate other decomposition processes that lead to a complete destruction of the CHF_3 molecule.

With the two technically most relevant hydroxides, KOH and NaOH, decomposition of CHF_3 can be effectively accomplished in the temperature range 420–470 K, *i.e.* at temperatures that are approximately 1000 K lower than those usually used for incineration. Decomposition of CHF_3 with KOH or NaOH under relatively very mild conditions could therefore represent a convenient and technically non-demanding process for the destruction of smaller amounts of CHF_3 in situations where economics of the process is not of prime importance.

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