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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 ($\sim$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