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On the Synthesis of Chlorine Pentafluoride

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SUMMARY

The reaction between chlorine trifluoride and elemental fluorine was studied in order to find the optimal reaction conditions for the synthesis of chlorine pantafluoride. It has been found that nickel difluoride is a very effective catalyst for the mentioned reaction. The obtained results are expressed as space–time–yield of chlorine pentafluoride.

INTRODUCTION

Several syntheses of chlorine pentafluoride have been published or patented, where chlorine trifluoride or alkali tetrafluorochlorates or alkali chlorides were fluorinated with elemental fluorine under pressure at elevated temperatures [1–6]. The main disadvantage of all these methods is a relatively low space–time yield (quantity of ClF_3 converted into ClF_5 per unit volume in unit time), due to either a relatively low yield of chlorine pentafluoride or to a long reaction time.

In the present work, the reaction between chlorine trifluoride and fluorine under pressure was studied with special regard to the influence of the reaction conditions such as the mole ratio $ClF_3 : F_2$, reaction temperature, initial pressure, and the presence of catalyst upon the space–time yield, in order to work out a suitable method for the preparation of chlorine pentafluoride.

RESULTS

The syntheses were carried out in a 100 ml nickel bomb to which a pressure gauge was attached over a bellows–type pressure transducer [7]. The bomb was tested hydrostatically up to 300 bar. In the weighed bomb a known amount of ClF_3 was condensed. After that the bomb was filled with fluorine up to the initial pressure (usually about 100 bar measured at 22°C) and put into an aluminum–block furnace heated to the reaction temperature. After the reaction had been completed, fluorine was pumped off at –183°C. The amount of bound fluorine was determined by weighing the bomb after pumping off the excess fluorine.

In order to determine the proper reaction temperature, some preliminary experiments at various temperatures 200°C, 250°C and 300°C, respectively, were made without addition of catalyst. The mole ratio $ClF_3 : F_2$ was 1 : 20 and the initial pressure (measured at 22°C) 102 bar. As expected, the reaction at 300°C was the fastest. However, in this case only about 75 % of ClF_3 were converted into ClF_5 because of the shifting of the equilibrium $ClF_3 + F_2 \rightleftharpoons ClF_5$ to the left with increasing temperature. At 250°C and 200°C the degree of conversion was considerably higher (over 90 %), and therefore subsequent experiments were made at this temperatures.

In order to increase the space–time yield of ClF_5, the quantity of ClF_3 was increased at the expence of excess fluorine and mole ratios $ClF_3 : F_2$ = 1 : 10, 1 : 5 and 1 : 2,5, respectively, were used. In spite of the longer reaction time in these cases the space–time yield is generally higher. Since the space–time yield depends predominantly on the rate of the reaction, an effort was made to increase it using nickel difluoride as a catalyst. In earlier work of our group concerning the catalytic influence of some metal fluorides upon the thermal reaction between xenon and fluorine [8], a very high catalytic effect of nickel difluoride was observed, and this compound has also been successfully applied in the reaction between ClF_3 and fluorine [9]. In the presence of NiF_2 with a surface of about 60 m^2 the reaction was 1.5 – 2 times faster. Additionally, some experiments with silver difluoride instead of nickel difluoride were made, but the catalytic effect observed was not as high as that with NiF_2, leaving aside the difficult characterization of AgF_2 (measurement of the specific surface area, etc.).

The experiments with the catalyst were carried out in similar way as previously described, except that 2 g of prefluorinated anhydrous NiF_2 with a specific surface area 33 m^2/g were put into the nickel bomb.

The results obtained are collected in Table 1.

TABLE 1.
Space–time yield of ClF_5 under various reaction conditions

Mole ratio $ClF_3:F_2$	Initial pressure (bar)	Temperature (°C)	Degree of conversion (%)	Reaction time (h)	Space-time yield (g/l.h)
1 : 2.5	102	200	87	6	32
		250	71	1.7	95
1 : 5	102	150	87	12	8
		200	98	2	54
		250	70	0.5	143
	56	200	87	2	24
1 : 10	102	200	100	1.5	38

As shown, under the conditions used, the highest space-time yield (143 g/l.h) was observed at 250°C with the mole ratio $ClF_3 : F_2$ = 1 : 5 and an initial pressure of 102 atm (measured at 22°C). However, in this case only about 70 % of ClF_3 was converted into ClF_5. Despite the lower space–time yield, for the laboratory scale preparation synthesis at 200°C and a mole ratio 1 : 10 or 1 : 5 seems to be more suitable, since under these conditions the conversion of ClF_3 into ClF_5 is practically complete.

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