Catalytic Liquid-phase Fluorination of Tetrachlorethene (PCE) with Titanium Antimony Mixed Halides

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A new catalyst consisting of a $TiCl_4$–$SbCl_5$ mixture with a molar composition Sb : Ti = 4 : 1 makes possible the fluorination of tetrachlorethene with liquid HF at 90 °C.

Tetrachlorethene (PCE) is a possible feedstock for the preparation of substitutes for CFCs. Its reaction with HF gives HCFCs,[1] see eqn. (1).

$$\begin{array}{lll} CCl_2{=}CCl_2 + HF \rightarrow CHCl_2{-}CCl_2F & \rightarrow CHCl_2{-}CClF_2 & \\ \qquad\qquad\qquad \text{HCFC 121} & \quad \text{HCFC 122} & \\ & \rightarrow CHCl_2{-}CF_3 & \\ & \quad\ \text{HCFC 123} & (1) \end{array}$$

In this multistage process the addition of HF to the heavily chlorinated double bond is the key step and requires a catalyst, traditionally a Lewis acid. For that purpose TaF_5[2] or oxides[3] such as Ta_2O_5 are reported to be active at 150 °C. We report that a mixture of $SbCl_5$, a strong Cl^- acceptor and $TiCl_4$ is a catalyst for the addition of HF to PCE and the subsequent F for Cl exchange. The reactions were carried out at 90 °C in liquid HF.

In a first series of experiments a 100 ml autoclave was charged with 0.05 mol $SbCl_5$ or 0.05 mol $SbCl_5$–$TiCl_4$ mixture. Then PCE 0.25 mol and HF were added sequentially. The mixture was heated at 90 °C. After an appropriate reaction time the autoclave was cooled to 0 °C, vented with dry nitrogen and the mixture was quenched with 50 ml H_2SO_4 6 mol dm^{-3}. The organic phase was dried and analysed by GPC. The results are reported in Table 1.

Table 1

			Selectivity (%)		
Catalyst[a]	HF (mol.)	Conversn. (%)	HCFC 121	HCFC 122	Other[b]
$SbCl_5$	0.3	32	55	9	26
$SbCl_5$	1	45	49	33	18
$SbCl_5$	1.5	35	45	30	25
$SbCl_5$	1.8	20	64	21	25
$SbCl_5$ Ti Cl_4[c]	1.0	65	43	33	24
$SbCl_5$ Ti Cl_4[c]	1.5	65	38	35	27
$SbCl_5$ Ti Cl_4[d]	1.4	22	58	5	37
$TiCl_4$	1.0	0			

[a] 0.05 mol. [b] CCl_3–CCl_3, $CHCl_2$–CCl_3, CCl_3–CCl_2F, CCl_2F–CCl_2F. [c] Sb : Ti = 4 : 1 (molar ratio). [d] Sb : Ti = 1 : 1 (molar ratio). T = 90 °C; P = 2 MPa; t = 4 h; $CCl_2 = CCl_2$ = 0.25 mol.

It is worth noting that the activity of $SbCl_5$ decreases when the amount of HF increases. $TiCl_4$ is inactive but its association with $SbCl_5$ increases the conversion whatever the amount of HF. The catalytic activity of this Sb–Ti system depends on the Sb : Ti molar ratio, with an optimum ratio of *ca.* 4 : 1. On the other hand, the selectivity towards the formation of HCFC 121 and 122 is around 75% because while the temperature is rising at the beginning of the experiment there is a partial decomposition of $SbCl_5$ into $SbCl_3$. It results in a chlorination of PCE and the resulting chlorinated alkane is afterwards fluorinated to give CCl_3–CCl_2F and CCl_2F–CCl_2F.

In order to prevent these side reactions a second series of experiments was carried out with a preprepared catalyst. For that purpose the autoclave was charged with the appropriate amount of $SbCl_5$ or $SbCl_5$–$TiCl_4$ mixture (0.05 mol.) and HF (2 mol.). After 1 h at 90 °C the autoclave was cooled at 30 °C and vented with dry nitrogen. PCE (0.25 mol.) and HF (2 mol.) were added and the reaction was performed as above mentioned. The results are reported in Table 2.

Table 2

			Selectivity (%)		
Catalyst[a]	HF (mol.)	Conversn. (%)	HCFC 121	HCFC 122	Other
$SbCl_5$[a]	2	48	29	63	8
$SbCl_5$ Ti Cl_4[b]	2	60	29	64	7
$SbCl_5$ $TiCl_4$[c]	2	31	59	36	5

[a] 0.05 mol. [b] Sb : Ti = 4 : 1 (mol ratio). [c] Sb : Ti = 1 : 1 (mol ratio). T = 90 °C; P = 2 MPa. t = 4h; $CCl_2 = CCl_2$ = 0.25 mol.

According to this procedure, the activity is unchanged but the selectivity is improved, and more than 90% HCFC are obtained.

In conclusion, the association of Sb with Ti affords a catalyst for the addition of HF to tetrachlorethene and the subsequent F for Cl exchange. The best composition is a Sb : Ti ratio of 4 : 1. This SbTi mixed fluoride provides a Lewis acid centre, presumably Ti^{3+},[4] and a F^- pool located on Sb. We have at present no explanation deemed worth reporting for the optimal Sb : Ti ratio.

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