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).

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

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

Catalyst[a]	HF (mol.)	Conversn. (%)	Selectivity (%) 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
$SbCl_5\,TiCl_4$[c]	1.0	65	43	33	24
$SbCl_5\,TiCl_4$[c]	1.5	65	38	35	27
$SbCl_5\,TiCl_4$[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.

Table 2

Catalyst[a]	HF (mol.)	Conversn. (%)	Selectivity (%) HCFC 121	HCFC 122	Other
$SbCl_5$[a]	2	48	29	63	8
$SbCl_5\,TiCl_4$[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.

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.

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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