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PRELIMINARY NOTE

Fluorination of Chlorofluoroethanes by Hydrogen [ $^{18}\text{F}$ ]-Fluoride in the Presence of a Chromia Catalyst

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SUMMARY

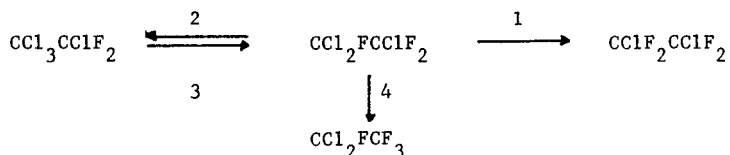
An  $^{18}\text{F}$  tracer study of the fluorination of  $\text{CCl}_2\text{FCClF}_2$  or  $\text{C}_2\text{Cl}_2\text{F}_4$  isomers by hydrogen fluoride over a chromia catalyst, indicates that a surface fluoride species is involved. The interaction of HF with chromia is substantial, and evidence for three different fluoride species is presented.

Despite widespread interest in the catalytic fluorination of chlorofluoroethanes by hydrogen fluoride under heterogeneous conditions [1-4], little is known about the interactions which occur at the surface of the catalyst. We have obtained direct evidence for the involvement of a surface fluoride species from a fluorine-18 ( $t_{1/2} = 110$  min) radiotracer study.

Flowing  $\text{H}^{18}\text{F}$  over a pelleted, commercial chromia catalyst, contained in a Monel metal reactor equipped with an F.E.P. counting tube, at 623K for 0.5h, results in uptakes of  $^{18}\text{F}$  activity which are equivalent to approximately  $1 \text{ mmol H}^{18}\text{F} (\text{g chromia})^{-1}$ . Flowing  $\text{CCl}_2\text{FCClF}_2$ , He mixtures over chromia, labelled with  $^{18}\text{F}$  in this way, for 0.5 h at 623K leads to the incorporation of 17-28% of the  $^{18}\text{F}$  activity in the chlorofluoroethane mixtures produced. Two of the components of the mixtures are [ $^{18}\text{F}$ ]- $\text{CClF}_2\text{CClF}_2$  and [ $^{18}\text{F}$ ]- $\text{CCl}_2\text{FCClF}_2$ , the specific activity of the former being greater than that of the latter. 64-71% of the activity

is retained by the solid. After extensive use, the fluorine and chlorine contents of the solid are 9.1 and 0.91 w/w% respectively, and its surface area has decreased from 66.5 to 22.0 m<sup>2</sup>g<sup>-1</sup>.

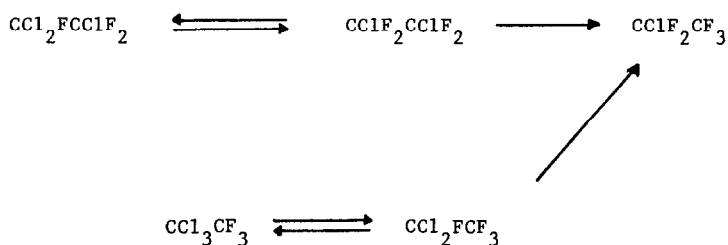
The behaviour of CCl<sub>2</sub>FCClF<sub>2</sub> under these conditions, determined from <sup>18</sup>F tracer experiments and G.C. and <sup>19</sup>F n.m.r. analyses of product mixtures, is summarised in Scheme 1. The most important reactions at this temperature are 1, 2 and 3. Reaction 1 leads to [<sup>18</sup>F]-CClF<sub>2</sub>CClF<sub>2</sub>, and must



Scheme 1

involve a surface fluoride species. This reaction presumably provides the chloride species required for reaction 2. The sequence of reactions, 2 then 3, accounts for the labelling of CCl<sub>2</sub>FCClF<sub>2</sub>.

Similar behaviour is observed between CClF<sub>2</sub>CClF<sub>2</sub> and [<sup>18</sup>F]-labelled catalyst at 698K. 19-22% of the <sup>18</sup>F originally present on the catalyst is incorporated in the chlorofluoroethane mixture produced. The C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub> used contained 7.8% CCl<sub>2</sub>FCF<sub>3</sub>, and the behaviour of both compounds is summarised in Scheme 2. <sup>18</sup>F labelling of CClF<sub>2</sub>CF<sub>3</sub> and C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub> is observed, the specific activity of the former being the greater.



Scheme 2

We conclude that the reactions involved are true surface processes, and that the overall reactions are best described by non-synchronous fluorination and chlorination steps. There is no evidence for isomerisation reactions in contrast to previous suggestions [2,4].

TABLE

Uptake of  $^{18}\text{F}$  by a chromia sample, and its removal by HF, both at 623K

$^{18}\text{F}$ or HF feed*	Flow time min.	Equivalent $\text{H}^{18}\text{F}$ uptake $\text{mmol g}^{-1}$	Chromia count rate		$^{18}\text{F}$ retained by chromia %
			before HF flow	after HF flow	
4.5	30	1.1	$1110 \pm 3$	$363 \pm 2$	33
2.5	20	0.8	$1058 \pm 3$	$437 \pm 2$	41
3.5	25	0.9	$1861 \pm 4$	$952 \pm 3$	51
4.0	25	1.0	$2478 \pm 5$	$1040 \pm 3$	42 <sup>†</sup>
4.0	25	1.25	$1303 \pm 4$	$787 \pm 3$	60 <sup>†</sup>
4.0	25	0.5	$2193 \pm 5$	$1698 \pm 4$	77 <sup>†</sup>
4.0	25	0.7	$1111 \pm 3$	$397 \pm 2$	35 <sup>†</sup>
4.0	25	0.9	$1271 \pm 4$	$540 \pm 2$	43 <sup>†</sup>

\* For a given experiment,  $\text{H}^{18}\text{F}$  and HF feeds and flow times were identical.† Sample pretreated with HF(g) prior to  $\text{H}^{18}\text{F}$  flow.

The behaviour of HF towards the chromia catalyst is complex, and the active fluoride species which participates in the reactions described above, is one of three types which can be distinguished by  $^{18}\text{F}$  tracer experiments. Approximately 10-15% of the  $^{18}\text{F}$  activity transferred to chromia by  $\text{H}^{18}\text{F}$  flow at 623K, is easily removed, for example by He flow for 0.5h at 623K. This fraction is considered to be present as weakly adsorbed HF. A greater proportion of  $^{18}\text{F}$  is removed by flowing inactive HF over [ $^{18}\text{F}$ ]-labelled catalyst and the results of a series of  $\text{H}^{18}\text{F}$  then HF flow experiments on the same catalyst sample are shown in the Table. Although the behaviour is somewhat variable over the series, in each case a significant proportion of  $^{18}\text{F}$  is removed, either by displacement or by exchange with HF.

In the early stages, treatment of the catalyst with HF is accompanied by a small mass decrease (ca.3%), the condensation of aqueous HF downstream from the reactor, and the almost complete (95%) removal of surface hydroxyl groups, the latter being determined by  $^1\text{H}/^2\text{H}$  exchange using mass spectrometric detection. Adsorption of HF, removal of bulk  $\text{H}_2\text{O}$  and the slow conversion of  $\text{Cr}^{\text{III}}\text{-OH}$  and  $\text{Cr}^{\text{III}}\text{-O}$  bonds to  $\text{Cr}^{\text{III}}\text{-F}$ , all appear to be important. The magnitude of  $^{18}\text{F}$  uptake indicates that both surface and bulk changes occur. Comparison with the behaviour of  $\text{CrF}_3$  towards  $\text{H}^{18}\text{F}$  at 623K, indicates that the retained  $^{18}\text{F}$ , which is inert to exchange with HF, is directly bound to  $\text{Cr}^{\text{III}}$ .

A plausible model of the catalytic halogen exchange involves the formation of active sites during the early part of the catalyst's life, and an equilibrium between weakly adsorbed HF and catalytically active fluoride. The latter is lost, either by reaction with the adsorbed chlorofluorocarbon, or by a reaction which leads to the formation of  $\text{Cr}^{\text{III}}\text{-F}$  bonds.

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