Role of chlorocarbon oligomers in the room-temperature heterogeneous catalytic fluorination of hydrochlorocarbons to hydrochlorofluorocarbons

Abdallah Bendada,[a] David W. Bonniface,[b] Fiona McMonagle,[a] Robert Marshall,[a] Caroline Shortman,[b] Ronald R. Spence,[a] James Thomson,[a] Geoffrey Webb,*[a] John M. Winfield*[a] and Neil Winterton[b]

[a] *Department of Chemistry, University of Glasgow, Glasgow, UK G12 8QQ*
[b] *Research and Technology Department, ICI Chemicals and Polymers Ltd, The Heath, Runcorn, UK WA7 4QD*

Radiotracer [^{18}F] and [^{36}Cl] experiments demonstrate the deposition of oligomeric chlorocarbon species on fluorinated metal oxides and trapping of hydrochlorocarbon monomers, both without loss of surface fluoride lability, thus accounting for the unusual room-temperature heterogeneous catalytic fluorination of CH_3CCl_3 and related species by anhydrous HF.

Recent fundamental studies of heterogeneous catalytic fluorination have been driven by the need to understand the catalytic routes to CFC alternatives such as CF_3CH_2F.[1] In most cases, catalytic fluorination of chloro- or hydrochloro-carbons by anhydrous HF occurs above 300 °C in the presence of fluorinated chromia[2] or γ-alumina.[3] When the hydrochlorocarbon undergoes facile dehydrochlorination, fluorination at *ambient temperature* is possible in the presence of catalysts, derived from fluorinated γ-alumina or chromia and conditioned prior to reaction by treatment with 1,1,1-trichloroethane, 1,1-dichloroethene or a related chlorocarbon.[4] Related behaviour has been demonstrated using fluorinated Fe_3O_4 and Co_3O_4.[5] These materials are termed oxide-supported organic layer catalysts and in this communication we account for their behaviour *via* the results of [^{18}F]-fluorine and [^{36}Cl]-chlorine radiotracer experiments.

Treatment of calcined γ-alumina with sulfur tetrafluoride, nominally at room temperature, results in an exothermic hydrolysis to give OSF_2, SO_2 and HF, the latter being retained by the solid. Fluorine contents up to *ca.* 15 mg atom F (g alumina)$^{-1}$ can be achieved by this procedure but there is no evidence for the formation of bulk metal(III) fluoride phases.[6] By analogy with chlorinated γ-alumina, fluorination should enhance both the Brønsted and Lewis acidity of the surface and room-temperature catalytic dehydrochlorination of CH_3CCl_3, with oligomerization of the product, $CH_2{=}CCl_2$, should be possible.[7] These reactions are observed but, unexpectedly, are accompanied by fluorination to give 1,1-dichloro-1-fluoroethane. Fluorinated chromia, derived from thermal decomposition of $(NH_4)_2Cr_2O_7$, followed by SF_4 treatment, behaves similarly, although *in situ* FTIR analyses of volatile products indicate that $CH_2{=}CCl_2$ and CH_3CCl_2F are formed in greater quantities over a 2 h period than is the case for fluorinated γ-alumina.

Extraction under anerobic conditions of the purple–brown material deposited on the surface of fluorinated γ-alumina followed by GCMS analysis, indicates that the organic layer contains highly chlorinated C_4, C_6 and C_8 species but that its fluorine content is negligible. The layer is unstable hydrolytically and loss of chlorine occurs on hydrolysis.

The fractions of [^{18}F] activity exchanged between γ-alumina, that has been fluorinated using SF_4, and $H^{18}F$, $SF_3{}^{18}F$ or $BF_2{}^{18}F$ at room temperature are very similar, and are substantial in all cases, although some degree of variation is apparent. Equally important is the observation that an organic layer has no inhibiting effect on the exchange (Table 1). Since the fluorine content of the layer itself is negligible, it is concluded, either that the [^{18}F]-labelled species diffuses readily through the layer, or that coverage of the fluorinated oxide surface is insufficient to block sites at which [^{18}F] exchange occurs. Similar behaviour is indicated for chromia although the study was limited to $BF_2{}^{18}F$.

In situ monitoring by a Geiger Müller counting technique,[8] of fluorinated surfaces derived from γ-alumina or chromia following the admission of [^{36}Cl]-labelled CH_3CCl_3, allows subsequent events occurring on the solid to be described. Laydown of organic material on both fluorinated γ-alumina and chromia occurs rapidly. Removal from the counting cell of material volatile at room temperature, leads to a decrease in the [^{36}Cl] count rate observed from the solid and this change is ascribed to the removal of weakly adsorbed [^{36}Cl]-CH_3CCl_3. Unexpectedly, when this surface is exposed subsequently to non-labelled HCl, the solid count rate increases slightly and [^{36}Cl]-labelled species, shown by FTIR to be a mixture of CH_3CCl_3 and CH_3CCl_2F, appear in the vapour phase. Separate experiments involving $H^{36}Cl$ established that HCl was adsorbed weakly both on fluorinated surfaces and on surfaces at which chlorocarbon oligomers had been deposited.

Table 1 [^{18}F]-Exchange reactions between γ-alumina samples and SF_4, BF_3 or HF

γ-Alumina fluorinated with SF_4[a]						γ-Alumina fluorinated with SF_4, conditioned with CH_3CCl_3[b]					
$SF_4{}^{18}F$/ mmol	f[c]	$BF_2{}^{18}F$/ mmol	f	$H^{18}F$/ mmol	f	$SF_3{}^{18}F$/ mmol	f	$BF_2{}^{18}F$/ mmol	f	$H^{18}F$/ mmol	f
0.97	0.53[d]	1.03	0.75	0.96	0.85	1.03	0.42	1.03	0.77	0.96	0.68
1.03	0.90	1.03	0.35	3.95	0.85	1.59	0.43	1.55	0.25	0.97	0.83
2.76	0.67	1.55	0.88	3.95	0.79	2.15	0.54	2.50	0.46	0.96	0.96
3.00	0.85	1.55	0.44			2.90	0.48	3.00	0.62	3.95	0.72
3.00	0.29	3.00	0.26			3.00	0.60	3.00	0.72	4.62	0.47

[a] Samples (0.5 g) fluorinated with 3 × 3.0 mmol aliquots of SF_4 in Monel; [b] then reacted with CH_3CCl_3 (3.0 mmol) for 1 h at room temp., in Monel. [c] Exchange factor f = 1 for complete exchange. [d] Errors ≤ ±0.06.

Absorption of radiation by neighbouring matter is a characteristic of β⁻-emitters, even those of moderately high energy like [^{36}Cl]. A direct result of the phenomenon is that β⁻ emission from [^{36}Cl]-labelled species migrating or trapped *within* the organic layer would not be detected and therefore the [^{36}Cl] activity detected is limited to those species *on the surface*. The observed change in the [^{36}Cl] surface count rate on exposure of the layer to HCl is therefore a result of events occurring *within* the layer and the observation of [^{36}Cl]-labelled CH_3CCl_3 and CH_3CCl_2F in the vapour phase indicates that these are hydrochlorination and hydrofluorination of [^{36}Cl]-$CH_2{=}CCl_2$ trapped in the layer. Also relevant are the observed turnover of [^{36}Cl]-activity when labelled CH_3CCl_3 interacts under flow conditions with γ-alumina which has been fluorinated then treated with [^{36}Cl]-CH_3CCl_3, and a previous observation[9] that CH_3CCl_3 and $CH_2{=}CCl_2$ are trapped within the organic layer formed on anhydrous aluminium(III) chloride.

It follows, therefore, that in the catalysed reaction of CH_3CCl_3 with HF, the latter replenishes the labile fluoride that is required for hydrofluorination of the intermediate $CH_2{=}CCl_2$, this species being formed at a strong Lewis acid site on the fluorinated oxide surface. However, the organic layer is also involved directly in the catalysis since it provides a quasi-liquid medium to trap CH_3CCl_3 and $CH_2{=}CCl_2$. The situation is a rare example of the promotion of catalytic activity by what can be regarded as coke precursors.

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