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Room-temperature Catalytic Fluorination of C_1 and C_2 Chlorocarbons and Chlorohydrocarbons on Fluorinated Fe_3O_4 and Co_3O_4

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A study of the room-temperature reactions of a series of C_1 and C_2 chlorohydrocarbon and chlorocarbon substrate molecules with fluorinated iron(II,III) oxide and cobalt(II,III) oxide has been conducted. The results show that fluorinated iron(II,III) oxide exhibits an ability to incorporate fluorine into the following substrates in the order: $Cl_2C{=}CCl_2 > H_2C{=}CCl_2 > CH_3CCl_3 > CHCl_3 > CH_2Cl_2 > CH_2ClCCl_3 > CCl_4 > CHCl_2CHCl_2$. The fluorinated cobalt(II,III) oxide gave the reactivity series $CHCl_3 > CCl_4 > H_2C{=}CCl_2 > CHCl_2CHCl_2 > CH_2Cl_2 > CH_3CCl_3 > CCl_2CCl_2 > CH_2ClCl_3$. Reactions of C_1 chlorohydrocarbon or chlorocarbon probe molecules with fluorinated Fe_3O_4 gave predominately C_1 chlorofluorohydrocarbon and chlorofluorocarbon products, respectively, whereas fluorinated cobalt(II,III) oxide produced predominately C_2 chlorofluorohydrocarbon and chlorofluorocarbons. For fluorinated Co_3O_4 the distribution of C_2 products obtained from C_1 chlorohydrocarbon precursor molecules is consistent with the formation of radical intermediates at strong Lewis acid surfaces. C_2 chlorohydrocarbons exhibit a fluorine for chlorine (F-for-Cl) exchange reaction through the catalytic dehydrochlorination of the substrate to the alkenic intermediate. The F-for-Cl exchange process was dependent upon the ability of the substrate material to undergo dehydrochlorination; the inability of a substrate to undergo dehydrochlorination results in the fluorination process proceeding through the formation of chlorocarbon or chlorohydrocarbon radical intermediates.

Chlorofluorocarbons (CFCs) are an important class of chemicals used in refrigeration, aerosol propellants, foam blowing and air conditioning.[1,2] There is an urgent requirement to find environmentally benign replacement hydrofluorocarbons (HFCs), and a renewed interest in the catalytic fluorination of chlorocarbons and related molecules has therefore recently emerged.[2] One of the methods for the industrial manufacture of the major CFC replacement HFC-134a (CH_2FCF_3) is reported to be by way of the hydrogenation of the CFC-114a (CCl_2FCF_3) intermediate using a carbon or aluminium(III) fluoride-supported palladium catalyst.[3-12] 1,1-Dichlorotetrafluoroethane (CFC-114a) is manufactured using a fluorinated chromia catalyst or a chromium(III) fluoride reagent from a feedstock of gaseous hydrogen fluoride and hexachloroethane (C_2Cl_6) or tetrachloroethene (C_2Cl_4) at temperatures of *ca.* 723 K.[13,14] Chromium-containing catalysts have potential carcinogenic properties, hence their landfill disposal is undesirable, and they are also subjects of import/export restrictions.

The catalytic preparation of CFCs under mild conditions has not been previously reported [the preparation of CFC intermediates normally involves high-temperature conditions (573–723 K)]. The use of fluorinated aluminium(III) oxide for low-temperature fluorination reactions is limited to chlorohydrocarbon substrate molecules as the reaction with chlorocarbon or CFC materials is not observed.[15] We have recently demonstrated that iron(II,III) oxide and cobalt(II,III) oxide are active towards the room-temperature fluorination of chlorocarbon and chlorohydrocarbon substrate compounds to give mixtures of chlorofluorohydrocarbons and chlorofluorocarbons.[16-18]

The ability of chlorohydrocarbons to undergo catalytic dehydrochlorination is dependent upon their thermal stability, which increases with the degree of chlorination, *e.g.* $CH_3CH_2Cl < CH_2ClCHCl_2 < CHCl_2CHCl_2$.[19] Furthermore, the abstraction of a hydrogen by a radical species is facilitated by progressive chlorination, *i.e.* $CH_3Cl < CH_2Cl_2 < CHCl_3$.[20] These two thermodynamic properties of chlorohydrocarbon substrate compounds are combined in the present study of the surface interaction of C_1 and C_2 chlorohydrocarbon and chlorocarbon compounds with fluorinated iron(II,III) and cobalt(II,III) oxides, respectively.

Experimental

Samples of high-purity iron(II,III) oxide and cobalt(II,III) oxide (Aldrich, 0.5 g) were pretreated by heating *in vacuo* at 523 K for 6 h. BET surface area determination using dinitrogen as adsorbate gave surface areas of 34.0 ± 2.1 and 30.9 ± 1.4 $m^2\ g^{-1}$ for the calcined Fe_3O_4 and Co_3O_4 catalysts, respectively.

Fluorination of the thermally conditioned samples was performed *in vacuo*, under static conditions, in a conditioned stainless-steel pressure vessel (Grade 316 steel, Hoke, 95 cm^3) using carbon tetrafluoride [Air Products, 8 mmol (g catalyst)$^{-1}$, 6 h] at 773 K. Volatile materials from the reaction, contained in an evacuable Pyrex cell fitted with AgCl windows, were identified using FTIR to be a mixture of CO_2, carbonyl fluoride (COF_2), unreacted CF_4 and silicon tetrafluoride. The SiF_4 indicates that anhydrous hydrogen fluoride is generated during the oxide fluorination process. Fluorine mass balance data gave a fluorine content of 3.3 and 3.4 mg atom† (g catalyst)$^{-1}$ for the iron(II,III) oxide and cobalt (II,III) oxide catalysts, respectively. Fluorinations of the Fe_3O_4 and Co_3O_4 oxides were also performed using sulfur tetrafluoride [SF_4, Air Products, 8 mmol (g catalyst)$^{-1}$] at 298 K *in vacuo* under static conditions in a conditioned stainless-steel pressure vessel containing thermally pretreated oxide samples. The volatile products were identified as thionyl fluoride, SO_2, SiF_4 and unreacted SF_4.

Freshly prepared samples of fluorinated iron or cobalt oxide (0.5 g) were reacted at room temperature *in vacuo* with aliquots of CH_3CCl_3, $H_2C{=}CCl_2$, CH_2ClCCl_2, $CHCl_2CHCl_2$, $Cl_2C{=}CCl_2$, CH_2Cl_2, $CHCl_3$, CCl_3CF_3, $CClF_2CCl_2F$ and CCl_4 [Aldrich, 7 mmol (g catalyst)$^{-1}$, 2 h]. The organic substrates were degassed by three pump–freeze–

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† 1 *g* atm = g/*M* where *M* is the relative atomic mass of the element.

thaw cycles, and stored *in vacuo*, under darkness, over activated 3A molecular sieves (Aldrich) contained in flamed-out Pyrex vessels fitted with PTFE stopcocks (J. Young). Bromination reactions were performed by condensing dibromine (2 mmol) with the organic substrate (4 mmol) at 77 K and warming the reaction mixture to room temperature, any unreacted dibromine being scrubbed from the reaction products with mercury. Volatile materials from the fluorination reactions were removed *in vacuo* and condensed onto dry NaF in a Pyrex vessel fitted with an NMR tube. The reaction products were identified using ^{19}F and ^{1}H NMR spectroscopy (Bruker AM200). ^{1}H chemical shifts were referenced to tetramethylsilane (TMS) and ^{19}F chemical shifts to trichlorofluoromethane (CFC-11).

Catalytic fluorination reactions were performed under static conditions by sequential addition of CCl_4 (3 mmol) and anhydrous hydrogen fluoride (1 mmol) *in vacuo* at 77 K into a conditioned stainless-steel bomb containing a sample of fluorinated Fe_3O_4 (0.5 g, fluorine content 1.65 mmol). The system was left to warm to room temperature. Temperature dependence studies were performed by heating the reaction vessel with an electrical furnace fitted with an Ni–Cr thermocouple. Preparation of the volatile material from the reaction for ^{19}F and ^{1}H NMR analysis was performed as described above.

Results

Reactions of Fluorinated Iron (II,III) Oxide

Results for the reactions of chlorocarbon and chlorohydrocarbon substrates with fluorinated Fe_3O_4 are presented in Tables 1 and 2. Table 1 shows the product distribution and yield of fluorinated products obtained from the various substrates and the fluorine utilisation of CFCs and HCFCs for each of the substrates investigated. Under the conditions used, complete utilisation of the fluorine component corresponded to the volatile material from the reaction having a total fluorine content of 47.1 g atom%. Data relating to the unchanged chlorocarbon or chlorohydrocarbon substrate material are not reported.

Calcined Fe_3O_4 did not induce dehydrochlorination of CH_3CCl_3 at room temperature. The room-temperature dehydrochlorination of CH_3CCl_3 on fluorinated Fe_3O_4, as evidenced by a singlet peak in the ^{1}H NMR spectrum at 5.5 ppm assigned to 1,1-dichloroethene (6.6 g atom%), indicates the generation of strong Lewis-acidic environments at the Fe_3O_4 surface by the fluorination process. The fluorine balance from the products corresponds to a 75% utilisation of available fluorine (Table 1). The volatile materials show a range of C_2 chlorofluorohydrocarbons, CH_3CCl_2F, CH_3CCl_2F and CH_3CF_3. Hydrochlorofluorocarbon and hydrofluoroalkane products accounted for 100% of the exchanged fluorine. No chlorofluorocarbon products from the reaction of CH_3CCl_3 with fluorinated Fe_3O_4 are detected. The presence of $H_2C{=}CF_2$ evidences the formation of alkenic material during the fluorination process. A small quantity of 1,1,1,2-tetrachloroethane (1.2 g atom%) is also present as reaction product, together with trace quantities of acetone. The interaction of the reaction product 1,1-dichloroethene ($H_2C{=}CCl_2$) with the fluorinated Fe_3O_4 was investigated and found to utilise 92.9% (Table 1) of the available fluorine. Volatile material consisted of predominately C_2 chlorofluorohydrocarbons, namely CH_3CCl_2F, CH_3CClF_2 and $CH_2ClCClF_2$. Chlorofluorocarbon material, $CClF_3$ and CCl_2FCClF_2, accounted for 22% of exchanged fluorine contained in the product material.

The effect of increasing the stability of the substrate towards dehydrochlorination was investigated by the reaction of fluorinated Fe_3O_4 with the substrate 1,1,1,2-tetrachloroethane (CH_2ClCCl_3). Analysis of the volatile material from the reaction revealed a mixture of chlorofluorohydrocarbon and chlorofluorocarbon products (Table 1), with relatively low fluorine utilisation (33.1% of available fluorine being incorporated into the reaction products). The major chlorofluorohydrocarbon product is CH_2ClCCl_2F followed by $CHCl_2CClF_2$. However, the chlorofluorocarbon $CClF_3$ contains 42% of the exchanged fluorine content. A further increase in the thermodynamic stability of the substrate towards dehydrochlorination by the reaction of 1,1,2,2-tetrachloroethane ($CHCl_2CHCl_2$) results in a further decrease in the fluorine utilisation to 24.2%. Analysis of the volatile reaction products shows that 81% of the exchanged fluorine is found in chlorofluorocarbon material (CCl_2FCClF_2 and CCl_3CF_3). The chlorofluorohydrocarbon CH_2ClCCl_2F accounted for the balance of the fluorinated products.

The reaction of the C_1 chlorohydrocarbons $CHCl_3$ and CH_2Cl_2 with fluorinated Fe_3O_4 gave fluorine utilisations of 51.4 and 41.8%, respectively. The reaction of chloroform produces mainly the C_1 chlorofluorocarbons CCl_3F and $CClF_3$, with the C_2 alkene $H_2C{=}CClF$. The chlorofluorocarbon fraction of the fluorinated products accounted for 62% of the exchanged fluorine. Non-fluorinated materials, acetone, dichloromethane and 1,1,2,2-tetrachloroethane, are also present in small or trace quantities in the product mixture. The substrate dichloromethane produces the C_2 chlorofluorohydrocarbons CH_2ClCCl_2F and $CHCl_2CClF_2$ on reaction with fluorinated Fe_3O_4. The major product $CClF_3$ contains 64% of the exchanged fluorine.

The interaction of the chlorocarbon substrates with fluorinated Fe_3O_4 was investigated with the reactions of $Cl_2C{=}CCl_2$ and CCl_4, respectively. The volatile material from the reaction of $Cl_2C{=}CCl_2$ gave the major product $CClF_3$, accounting for 44% of the total exchanged fluorine. The C_2 fluorinated products were all chlorofluorohydrocarbons, namely CH_2ClCCl_2F, $CH_2ClCClF_2$, $CHCl_2CF_3$ and CHF_2CF_3. Fluorine utilisation for the C_2Cl_4 substrate was found to be 100%. The reaction of CCl_4 with fluorinated Fe_3O_4 produced a range of C_1 chlorofluorocarbons (Table 1). The major product, CCl_3F, accounted for 63% of the exchanged fluorine; however, the reactivity of CCl_4 is relatively low, accounting for 29% of the fluorine utilisation. The reaction of CCl_4 with the fluorinated Fe_3O_4 was also performed in the presence of dibromine. ^{19}F NMR analysis confirmed the major product from this reaction to be CCl_2BrF (98%), with trace quantities of $CClF_3$ and $CClBrF_2$.

The fluorine-promoted Fe_3O_4 surface also induces room-temperature isomerisation of chlorofluorocarbons; C—C bond cleavage of chlorofluorocarbon substrates is also displayed by the fluorinated Fe_3O_4 surface. The reaction of CCl_2FCClF_2 with the fluorinated material gave $CClF_3$ (2 g atom%) and CCl_3CF_3 (2 g atom%). The reaction of the isomer CCl_3CF_3 at room temperature with the fluorine-promoted surface gave $CClF_3$ (4 g atom%), and 1,1-dichlorotetrafluoroethane (CCl_2FCF_3; 1 g atom%).

The product selectivity for the catalytic reaction of CCl_4 with anhydrous hydrogen fluoride on fluorinated Fe_3O_4 as a function of temperature is presented in Table 2. The presence of anhydrous hydrogen fluoride with substrate CCl_4 at room temperature gives a greater selectivity to $CClF_3$ (Table 2, selectivity 36%) relative to that obtained for the contact reaction of CCl_4 with the treated Fe_3O_4, where only trace quantities of $CClF_3$ are obtained (Table 1). The most notable feature of the product analysis is the presence of the C_2 chlorofluorocarbons CCl_2FCClF_2 (Table 2, selectivity 21.5%) and CCl_3CF_3 (selectivity 40%). The contact reaction of CCl_4

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with fluorinated Fe_3O_4 gives only C_1 chlorofluorocarbons (Table 1). An increase in the reaction temperature to 323 K increases the selectivity of the reaction for $CClF_3$ (80.5%). The optimum reaction temperature of 373 K was found to maximise the selectivity of the reaction of CCl_4 with HF to CCl_3CF_3 (78.5%), any further increase in reaction temperature resulting in a wider distribution of reaction products.

The results for the catalytic fluorination of CCl_4 with HF on a fluorinated Fe_3O_4 sample at 373 K under static conditions are also presented in Table 2. The selectivity to $CClF_3$ is increased to 19% at the expense of the C_2 chlorofluorocarbons (Table 2). However, further exposure of the catalyst to the reactant mixture increases the selectivity of the catalyst to CCl_3CF_3 which is the sole fluorinated product identified during runs 3 to 5. Thereafter, the selectivity to CCl_3CF_3 decreases until by run 7 only $CClF_3$ is identified. These results confirm the ability of fluorinated Fe_3O_4 material to catalyse the fluorination of CCl_4 to C_2 chlorofluorocarbons at relatively low reaction temperatures.

Reactions of Fluorinated Cobalt(II,III) Oxide

Product distributions for the reactions of chlorocarbon and chlorohydrocarbon substrates with fluorinated Co_3O_4 and the fluorine utilisation of CFCs and HFCs for each of the substrates used are presented in Table 3. Under the conditions employed, complete utilisation of fluorine from the catalyst surface produces 56.7 g atom% of fluorinated products.

The room-temperature reaction of 1,1,1-trichloroethane with calcined Co_3O_4 invoked the dehydrochlorination of CH_3CCl_3 to give $H_2C{=}CCl_2$ and gaseous HCl, the alkene subsequently polymerising on the dehydrated Co_3O_4 surface to build up a black tarry deposit. The ability of the calcined Co_3O_4 to dehydrochlorinate the CH_3CCl_3 at room temperature indicates that Lewis acid environments are present on the dehydroxylated Co_3O_4 material. The room-temperature reaction of CH_3CCl_3 with fluorinated Co_3O_4 results in the major fluorinated product CH_3CCl_3F with the minor product $CClF_3$. The dehydrochlorination product, $H_2C{=}CCl_2$, was also present indicating that dehydrochlorination of the substrate also occurred at the fluorinated surface. Fluorine utilisation for the 1,1,1-trichloroethane system was found to be low, relative to the fluorinated Fe_3O_4 system, at 24.1%. Of the exchanged fluorine, 74% was found in the CH_3CCl_2F fraction, and 26% in the chlorofluorocarbon $CClF_3$ (Table 3). Investigation of the interaction of the dehydrochlorination product 1,1-dichloroethene with the fluorinated Co_3O_4 results in an increase in fluorine utilisation to 53.1%, to give a mixture of chlorofluorohydrocarbon and chlorofluorocarbons. The major chlorofluorohydrocarbon products are CH_3CCl_2F and CH_3CClF_2, accounting for, in total, 64% of the exchanged fluorine. The minor products produced by the system were the C_2 CFCs, CCl_2FCClF_2 and the isomer CCl_3CF_3.

An increase in the thermodynamic stability of the substrate towards dehydrochlorination, leads to a decrease in the fluorine utilisation. An investigation of the reactivity of 1,1,1,2-tetrachloroethane gives a lower fluorine utilisation at 19.6%. The products from the reaction, CH_2ClCCl_2F, $CH_2ClCClF_2$ and $CClF_3$, show that 48.5% of the exchanged fluorine is contained in the chlorofluorohydrocarbon fraction, and 51.5% in the chlorofluorocarbon fraction. Increasing the thermodynamic stability of the substrate towards dehydrochlorination further, by the reaction of the isomer 1,1,2,2-tetrachloroethane, gives the chlorofluorocarbons $CClF_3$ and CCl_2FCClF_2, with $CH_2ClCClF_2$ as the minor component. Fluorine utilisation increases to 30.2%. Exchanged fluorine is distributed at 10.6% and 89.4% for chlorofluorohydrocarbons and chlorofluorocarbons, respectively.

Reactions of the C_1 chlorohydrocarbons $CHCl_3$ and CH_2Cl_2 with fluorinated Co_3O_4 give contrasting product materials. The volatile material from the reaction of $CHCl_3$ comprises mainly the C_2 CFCs, CCl_2FCClF_2, $CClF_2CClF_2$, CCl_3CF_3 and $CClF_3$. Fluorine utilisation for the system is 98.5%, of which C_2 CFCs account for 74% of the exchanged fluorine. The non-fluorinated materials, 1,1-dichloroethene and 1,1,1-trichloroethane were also present in small quantities in the product mixture. Dichloromethane gives the lowest fluorine utilisation of the C_1 substrates investigated at 29.3%, the fluorine content of the CFCs accounting for 88% of the exchanged fluorine. 1,1-Dichloroethene was also observed in the product mixture from the reaction of CH_2Cl_2.

The reactions of chlorocarbons with fluorinated Co_3O_4 were also investigated. The reaction of tetrachloroethene with the fluorinated Co_3O_4 material produced a fluorine utilisation of 21.9%. In contrast to the fluorinated Fe_3O_4 system, the reaction produced only chlorofluorocarbons, namely CCl_3F and $CClF_2CClF_2$. Interaction of CCl_4 also gave uniquely CFC materials, CCl_3CF_3, CCl_2FCClF_2, $CClF_3$ and CCl_3F. The reaction gave rise to 56.9% fluorine utilisation, of which the C_2 products accounted for 67% of the exchanged fluorine. Non-fluorinated materials, 1,1-dichloroethene and 1,1,1-trichloroethane were also present in the reaction mixture in small or trace quantities. The reaction of CCl_4 with fluorinated Co_3O_4 in the presence of dibromine was also conducted. ^{19}F NMR analysis confirmed the presence of the major product CCl_2BrF (99%) with trace quantities of $CClF_3$ and $CClBrF_2$.

The fluorine-promoted surface also demonstrates an ability to isomerise CCl_2FCClF_2 to CCl_3CF_3 (5 g atom%) at room temperature. For the reaction of CCl_2FCClF_2 with the fluorinated surface, the reaction products $CClF_3$(<1 g atom%) and C_2F_6 (<1 g atom%) are also detected.

Discussion

The reactions described above can be broadly attributed to fluorine for chlorine exchange. However, the room-temperature exchange reactions demonstrated by the fluorine-promoted Fe_3O_4 and Co_3O_4 systems to give chlorofluorocarbons or chlorofluorohydrocarbons occur at temperatures far lower than that required for F-for-Cl exchange on chromia which occurs at *ca.* 600–700 K.[19] Room-temperature halogen-exchange reactions using fluorinated γ-alumina that produce chlorofluorohydrocarbons have been reported; however, the production of chlorofluorocarbons at ambient temperatures is not observed.[15,21] The dehalogenation of chlorohydrocarbons by iron or cobalt salts has received little attention, although the reaction of iron(II) chloride with CCl_4 is well established,[22] showing the formation under anhydrous conditions of $^{\cdot}CCl_3$ species and iron(III) chloride. In the presence of an alkene the $^{\cdot}CCl_3$ radical and $^{\cdot}Cl$ moieties formed, add across the double bond.[23]

The reactivity of the fluorinated iron(II,III) oxide towards the fluorination of chlorohydrocarbon and chlorocarbon C_1 and C_2 substrate molecules (Table 1) differs from that exhibited by fluorinated cobalt(II,III) oxide (Table 3). The fluorinated iron(II,III) oxide catalyst demonstrates that the reactivity towards fluorine incorporation into chlorohydrocarbon or chlorocarbon substrates is

$$Cl_2C{=}CCl_2 > H_2C{=}CCl_2 > CH_3CCl_3 >$$
$$CHCl_3 > CH_2Cl_2 > CH_2ClCCl_3 > CCl_4 > CHCl_2CHCl_2.$$

Table 1 Reaction of fluorinated iron (II,III) oxide with C_1 and C_2 chlorohydrocarbons or chlorocarbons

	product distribution (g atom%)															
substrate reagent	CH_3CCl_2F	CH_3CClF_2	CH_3CF_3	$H_2C{=}CF_2$	$CH_2ClCClF_2$	CCl_2FCClF_2	$CClF_3$	CH_2ClCCl_2F	CCl_3CF_3	$CHCl_2CF_3$	CHF_2CF_3	CCl_3F	$H_2C{=}CClF$	fluorine used (%)	HCFCs (%)	CFCs (%)
CH_3CCl_3	21.0	3.0	1.5	2.0										75.0	100.0	0.0
$H_2C{=}CCl_2$	8.0	10.1			3.0	1.0	2.2							92.9	78.0	22.0
CH_2ClCCl_3					1.0		2.2	7.0						33.1	58.0	42.0
$CHCl_2CHCl_2$						2.0		2.1	1.1					24.2	19.0	81.0
$Cl_2C{=}CCl_2$					2.1		9.2	2.0		3.1	2.2			100.0	56.0	44.0
$CHCl_3$							4.0					3.1	9.1	51.4	62.0	38.0
CH_2Cl_2					2.0		4.2	3.1						41.8	64.0	0.0
CCl_4							4.3					5.1		29.1	0.0	100.0

Table 2 Effect of temperature on the reaction of HF and CCl_4 over fluorinated iron(II,III) oxide

		selectivity to fluorinated products (%)				
reaction temperature/K	catalytic run	$CClF_3$	CCl_2FCClF_2	CCl_3CF_3	CCl_3F	CCl_2FCCl_2F
298		36.0	21.5	40.0		
323		80.5	7.5	11.0		
373		6.5	13.0	78.5		
	1	19.0	7.5	72.0		
	2	0.5	16.0	83.0		
	3			100.0		
	4			100.0		
	5			100.0		
	6		17.0	60.0	11	11
	7	99.0		1.0		

Table 3 Reaction of fluorinated cobalt(II,III) oxide with C_1 and C_2 chlorohydrocarbons or chlorocarbons

	product distribution (g atom%)																		
substrate reagent	CH_3CCl_2F	CH_3CClF_2	CH_3CF_3	$H_2C{=}CF_2$	$CH_2ClCClF_2$	CCl_2FCClF_2	$CClF_3$	CH_2ClCCl_2F	CCl_3CF_3	CCl_2FCClF_2	CHF_2CF_3	CCl_3F	$H_2C{=}CClF$	CCl_2F_2	CF_4	fluorine used (%)	HCFCs (%)	CFCs (%)
CH_3CCl_3	10.1						1.2									24.1	74.0	26.0
$CH_2{=}CCl_2$	10.3	4.8	0.1			1.2			2.2							53.1	66.1	33.9
CH_2ClCCl_3				0.1	1.2		1.9	3.0								19.6	48.5	51.5
$CHCl_2CHCl_2$						2.2	2.9	1.8								30.2	10.6	89.4
$Cl_2C{=}CCl_2$						2.3						3.2				21.9	0.0	100.0
$CHCl_3$						5.0	4.9		6.2	1.9			0.1			98.5	0.0	100.0
CH_2Cl_2						1.0	3.9	1.9								29.3	11.6	88.4
CCl_4							2.9		5.1	2.1		2.0		0.1	0.1	56.9	0.0	100.0

The fluorinated cobalt(II,III) oxide displays the reactivity series:

$$CHCl_3 > CCl_4 > H_2C{=}CCl_2 > CHCl_2CHCl_2 > CH_2Cl_2 > CH_3CCl_3 > Cl_2C{=}CCl_2 > CH_2ClCCl_3.$$

In all cases except $CHCl_3$, fluorine utilisation was found to be greater for the fluorinated Fe_3O_4 than for fluorinated Co_3O_4 (Tables 1 and 3).

The product distribution for the room-temperature reaction of C_2 chlorohydrocarbon substrates with fluorinated iron oxide reflects the thermodynamic stability of the substrate to dehydrochlorination. The reactivity series for the Fe_3O_4 system is $CH_3CCl_3 > CH_2ClCCl_3 > CHCl_2CHCl_2$ and is consistent with this hypothesis. The presence of $H_2C{=}CCl_2$ and $H_2C{=}CF_2$ as minor products from the reaction of CH_3CCl_3 with the fluoro–iron–oxo hydroxy material confirms that haloalkenic material is generated during the halogen-exchange reaction. Thermally pretreated Fe_3O_4 did not show any reaction with CH_3CCl_3 at room temperature, but the ability of the fluorinated Fe_3O_4 to dehydrochlorinate CH_3CCl_3 at room temperature confirms the generation of strong Lewis-acidic environments at the oxide surface by the fluorination process.

Results from the fluorinated Fe_3O_4 system show that the ratio of fluorine incorporation into saturated chlorohydrocarbons also corresponds to the ability of the substrate to undergo dehydrochlorination. The results show the fluorine incorporation in chlorofluorohydrocarbon products to be in the order $CH_3CCl_3 > CH_2ClCCl_3 > CHCl_2CHCl_2$ at 75%, 33.1% and 24.2%, respectively (Table 1). The products from the fluorination reaction show that all exchanged fluorine is found on the α-carbon, a result which is consistent with the halogen-exchange mechanism proceeding through the formation of a carbocation intermediate species.

As the thermal stability of the substrate towards dehydrochlorination is increased, the fluorine component contained within the chlorofluorocarbon products in the reaction mixture also increases. Reaction of fluorinated Fe_3O_4 with CH_3CCl_3 gives no chlorofluorocarbon products, whereas CFC products obtained from CH_2ClCCl_3 and $CHCl_2CHCl_2$ substrates, respectively, account for 42% and 81% of the exchanged fluorine. Furthermore, $CClF_3$ is also found as a reaction product from the C_2 substrate, confirming that the Lewis-acidic surface is sufficiently electrophilic to cause bond fission, a process fundamental to the formation of radical species. The generation of radical species from chlorocarbons at the fluorinated Fe_3O_4 surface is supported by the identification of CCl_3CF_3 as the sole reaction product during the catalytic fluorination of CCl_4 in the presence of anhydrous hydrogen fluoride (Table 2). The presence of the C_2 chlorofluorocarbons CCl_2FCClF_2 and CCl_3CF_3 is observed at 373 K, and as the catalyst is worked the selectivity to CCl_3CF_3 increases to 100%.

The reaction of the alkenes $Cl_2C{=}CCl_2$ and $H_2C{=}CCl_2$ with fluorinated Fe_3O_4 to give chlorofluorohydrocarbon and chlorofluorocarbon products occurs with a fluorine utilisation of 92.9% (Table 1). Both of these substrates can form an adsorbed unsaturated intermediate at the Lewis-acidic surface without undergoing the initial dehydrochlorination reaction. The major products from the reaction of $H_2C{=}CCl_2$ with fluorinated Fe_3O_4 are CH_3CCl_2F and CH_3CClF_2. The presence of these products is consistent with hydrofluorination of the alkene substrate, by the adsorbed HF produced from the initial fluorination treatment of the catalyst with SF_4 or CF_4. The adsorbed hydrogen fluoride is generated *in situ* from the hydrolysis of SF_4 or SOF_2, or the reaction product COF_2, where CF_4 is the fluorinating reagent, with surface hydroxy groups. Again, all exchanged fluorine is found on the α-carbon, which is consistent with the halogen-exchange mechanism proceeding through the formation of a surface-adsorbed carbocation intermediate.

The substrate $Cl_2C{=}CCl_2$ gives chlorofluorohydrocarbons in a small excess yield to chlorofluorocarbons, with a fluorine distribution of 44% in the CFC fraction. Here fluorine utilisation for the alkene material is high at 100%. The high mole fraction of $CClF_3$ in the reaction products (Table 1) is consistent with the formation of a C_1 radical intermediate during the adsorption process.

The fluorinated Co_3O_4 system displays a different reactivity series to that of the fluorinated Fe_3O_4 catalyst (Table 3). The reactivity based on fluorine utilisation is

$$CHCl_3 > CCl_4 > H_2C{=}CCl_2 > CHCl_2CHCl_2 > CH_2Cl_2 > CH_3CCl_3 > Cl_2C{=}CCl_2 > CH_2ClCCl_3.$$

Examination of the fluorine utilisation data for the CFC fraction shows

$$CHCl_3 = CCl_4 = Cl_2C{=}CCl_2 > CH_2Cl_2 = CHCl_2CHCl_2 > CH_2ClCCl_3 > H_2C{=}CCl_2 > CH_3CCl_3.$$

It is clear that the fluorinated Co_3O_4 surface displays a greater affinity for generation of CFCs from the same range of substrate materials than the fluorinated Fe_3O_4 material. The fluorinated Co_3O_4 system shows that an increase in the thermodynamic stability of the chlorohydrocarbon substrate towards dehydrochlorination will result in a greater yield of chlorofluorocarbon material relative to the chlorofluorohydrocarbon fraction. The product distributions from the room-temperature reactions of the C_1 substrate materials with fluorinated Fe_3O_4 and Co_3O_4, respectively, reveals the chemistry occurring at these active surfaces.

The fluorinated Fe_3O_4 system when reacted with the C_1 substrates CCl_4 and $CHCl_3$ produces mainly C_1 fluorinated products. In contrast, the fluorinated Co_3O_4 gives noticeable excess quantities of C_2 compounds for the same C_1 substrates. The products obtained from reaction of $CHCl_3$ or CCl_4 with fluorinated Co_3O_4 were CCl_2FCClF_2 and the isomer CCl_3CF_3, which is consistent with the formation of the same adsorbed intermediate species from both substrates. The reactions of chlorofluorocarbons at ambient temperatures with the fluorinated oxides have shown that the CCl_2FCClF_2 so formed can react with the fluorinated Fe_3O_4 or Co_3O_4 to undergo isomerisation to CCl_3CF_3. Analysis of the product distributions obtained from the fluorinated Fe_3O_4 and Co_3O_4 surfaces shows that $CClF_3$ is produced over wide range of C_2 substrate materials, thus demonstrating the ability of the fluorinated oxides to initiate bond fission (Tables 1 and 3). The high proportion of $CClF_3$ obtained across the range of substrates examined indicates that fluorine substitution into an adsorbed chlorine-containing radical intermediate is a fast process, relative to the formation of the initial C_1 fragment. The same products are also obtained from reaction of $CHCl_2CHCl_2$ or CH_2Cl_2 with the fluorinated Co_3O_4. Both substrates give the same reaction products (Table 3, CH_2ClCCl_2F, CCl_2FCClF_2 and $CClF_3$), fluorine utilisation values and product distributions through the HCFCs and CFCs. These observations are again consistent with the same reaction intermediate being formed during substrate adsorption at the fluorinated oxide surface. We propose that the adsorbed species from the $CHCl_2CHCl_2$ and CH_2Cl_2 substrates is $^{\cdot}CHCl_2$, formed through bond polarisation of the adsorbed material. The high ratio of C_2

materials from reaction of C_1 substrates with fluorinated Co_3O_4 is also consistent with the respective intermediate compound being a radical species. The reaction of CCl_4 with fluorinated Co_3O_4 in the presence of dibromine is consistent with this hypothesis. The fluorinated Fe_3O_4 material on reaction with CCl_4 produces mainly C_1 fluorinated products, but for the fluorinated Co_3O_4 system the products from the reaction of CCl_4 are mainly C_2 chlorofluorocarbons. Addition of dibromine to CCl_4 prior to reaction with fluorinated Co_3O_4, suppresses the formation of C_2 products to give solely C_1 compounds, the major product being CCl_2BrF. The dibromine in the reaction mixture is a source of potential radical species and hence is available for termination of radical propagation.

The observed reaction of chlorine-containing substrates with fluorinated Co_3O_4 is in contrast to that observed for the fluorinated Fe_3O_4 system. Fluorinated Fe_3O_4 displays a reduced ability to produce C_1 products from C_2 chlorohydrocarbons or chlorocarbon substrates, and a reduced ability to form C_2 products from C_1 chlorohydrocarbons or chlorocarbons relative to the fluorinated Co_3O_4. The room-temperature reaction of CCl_4 with the fluorinated Co_3O_4 oxide gives CCl_2FCClF_2, CCl_3CF_3 and $CClF_3$ as reaction products and minor quantities of CCl_3F, whereas the fluorinated Fe_3O_4 gives CCl_3F and CCl_2F_2 with no $CClF_3$ or C_2 compounds. The results suggest that the fluorinated Fe_3O_4 oxide exhibits a reduced ability to induce radical formation, or is itself an unstable radical initiator, relative to the fluorinated Co_3O_4 material. These observations can be accounted for by the ability of the Fe^{3+} environments to undergo a redox reaction with the radical substrate through a one-electron transfer to an Fe^{2+} species. The morpho-electronic properties of the inverse spinel structure of the Fe_3O_4 material can assist in this process of electron transfer. In the solid, all of the Fe^{2+} ions are present in octahedral environments together with half of the Fe^{3+} ions. This structure results in a rapid valence oscillation between the Fe^{II} and Fe^{III} environments, as exemplified by the enhanced conductivity of Fe_3O_4 relative to Fe_2O_3. The Co_3O_4 material, having a spinel structure, has all of the Co^{2+} species in tetrahedral environments with the Co^{3+} species in the octahedral positions.

Conclusions

Fluorinated Fe_3O_4 and Co_3O_4 are active catalysts for the low-temperature preparation of chlorofluorocarbons and chlorofluorohydrocarbons from halocarbon and halohydrocarbon substrates with anhydrous hydrogen fluoride. The treated iron (II,III) oxide displays catalytic properties that can be used in the preparation of chlorofluorohydrocarbons and C_1 chlorofluorocarbons at low temperatures. Fluorinated Co_3O_4 exhibits catalytic properties that can be used preferentially for the preparation of C_2 chlorofluorocarbons. The surface reaction of chlorohydrocarbons with fluorinated Fe_3O_4 is dependent upon the ability of the organic substrate to undergo dehydrochlorination. An increase in the thermodynamic stability of the substrate towards dehydrochlorination results in the fluorination process proceeding *via* the formation of radical intermediates. Fluorinated Co_3O_4 exhibits a greater tendency to form radical intermediates from halocarbons or halohydrocarbons relative to fluorinated Fe_3O_4 material.

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