Generation of radical species in surface reactions of chlorohydrocarbons and chlorocarbons with fluorinated gallium(III) oxide or indium(III) oxide

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The reactions of C_1 and C_2 chlorohydrocarbons and chlorocarbons have been studied with the Lewis acid catalysts fluorinated gallium(III) oxide and fluorinated indium(III) oxide, respectively. Product analysis shows chlorine-for-fluorine exchange reactions together with the formation of 2-methylpropane and its chlorinated analogues 2-chloromethyl-1,3-dichloropropane and 2-chloromethyl-1,2,3-trichloropropane. Reactivities of the chlorohydrocarbon probe molecules show fluorinated gallium(III) oxide to be a stronger Lewis acid than fluorinated indium(III) oxide. The formation of the symmetrical butyl compounds is consistent with the generation of surface radical species and is also consistent with a 1,2-migration mechanism operating within radical moieties at the Lewis acid surface.

The interaction of chlorocarbons with Lewis acid catalysts has been studied over many years, as chlorocarbons are used as precursor compounds in the industrial preparation of chloro-fluorocarbons and hydrofluoroalkanes.[1–12] The literature abounds with the ionogenic reaction of halocarbons and halohydrocarbons, through the formation of the classical Friedel–Craft species in conjunction with a wide variety of metal halide acid catalysts.[13–18] With regard to Friedel–Crafts catalysts, the vast bulk of the literature proposes the formation of products through carbocation intermediates, which are generated by (i) heterolytic bond fission of a halo-carbon substrate at Lewis acid sites,[18] or (ii) addition of a functional group to an sp^2 hybridized carbon, with the sub-sequent formation of the respective carbocation interme-diate.[18]

Solid/gas reactions that have reported the generation of radical species are rare. However, Rooney and Pink[19] con-cluded that free radical active intermediates were produced in the ring closure step during the formation of naphthalene in the presence of aluminium(III) chloride or aluminium(III) bromide during the liquid phase reaction of aromatic hydro-carbons.[19] It has also been reported that antimony(V) pen-tachloride and tin(IV) tetrachloride catalyse the reactions of mono- or di-alkylbenzene with benzylic halides through a free radical mechanism.[20]

In our previous studies of the chlorine-for-fluorine (Cl-for-F) exchange reactions of chlorohydrocarbons and chlorocarb-ons on fluorinated iron(II,III) oxide and cobalt(II,III) oxide, respectively, we have reported the formation of fluorocarbon and fluorohydrocarbon products that are consistent with the generation of radical species at the catalyst surface.[4] The present study now reports the formation of surface adsorbed radical species, from C_1 chlorohydrocarbons, during the het-erogeneous reaction of a series of chlorocarbon and chlorohy-drocarbon compounds with fluorinated gallium(III) and indium(III) oxides, respectively.

Experimental

Samples of β-gallium(III) oxide and indium(III) oxide (0.5 g, 2.7 mmol, Johnson Matthey) were pretreated by heating *in vacuo* at 523 K for 6 h. Fluorination of the thermally conditioned oxides was also performed *in vacuo*, under static conditions, in a conditioned stainless-steel pressure vessel [Grade 316 steel, Hoke, 95 cm³, using sulfur tetrafluoride (8.0 mmol g(catalyst)$^{-1}$, Air Products) at room temperature. After a 20 min reaction period the sample was degassed by pumping for 30 min. A further aliquot of SF_4 (8 mmol) was condensed over the cata-lyst sample at 77 K and then allowed to warm to room tem-perature and react for 90 min. Volatile materials from the fluorination stage were transferred into a specially designed Pyrex gas cell fitted with AgCl windows. Using FTIR, these compounds were identified as a mixture of thionyl fluoride, sulfur dioxide and silicon tetrafluoride (generated from the reaction of anhydrous hydrogen fluoride with Pyrex vessel). The fluorinated catalyst samples were degassed by pumping for 30 min prior to a further aliquot of SF_4 (8 mmol) being transferred to the reaction vessel. Fluorination of the oxide sample was continued until excess SF_4 was identified in the IR by a peak at 984 cm^{-1}. Catalyst pretreatment was completed by pumping the sample for 30 min at room temperature.

Freshly prepared samples of fluorinated gallium(III) oxide or indium(III) oxide were reacted *in vacuo* under darkness, at room temperature with aliquots of 1,1,1-trichloroethane, 1,1-dichloroethene, sym-tetrachloroethane, asym-tetrachloro-ethane, tetrachloroethene, methylene chloride, chloroform, carbon tetrachloride, 1,1,2-trichlorotrifluoroethane, or 1,1,1-trichlorotrifluoroethane (Aldrich, 7 mmol g(catalyst)$^{-1}$, 2 h). Organic precursors were degassed by three pump–freeze–thaw cycles, and stored *in vacuo* in darkness, over activated 3 Å molecular sieves (Aldrich), contained in previously flamed-out Pyrex vessels, fitted with PTFE stopcocks (J. Young). Volatile materials from the reaction mixture were removed *in vacuo* and condensed onto dry NaF in a Pyrex vessel fitted with an NMR tube. Reaction products were identified using ^{1}H and ^{19}F NMR spectroscopy (Bruker AM200). ^{1}H chemical shifts were referenced to tetramethylsilane (TMS) and ^{19}F chemical shifts to trichlorofluoromethane (CFC-11). Volatile material was condensed at 77 K onto dry, degassed deuterochloroform solvent and sealed *in vacuo* in an NMR side arm. Mass spec-troscopy was performed using a VG Analytical 11-250J mass spectrometer.

Results

Results of the product distribution for the room temperature

reaction of chlorocarbons and chlorohydrocarbons with fluorinated gallium(III) oxide and fluorinated indium(III) oxide are presented in Tables 1 and 2, respectively. Both fluorinated gallium oxide and fluorinated indium oxide react with 1,1,1-trichloroethane. Fluorinated gallium oxide gives 1,1,-dichloro-1-fluoroethane (12 mol.%), 1-chloro-1,1-difluoroethane (3 mol.%) , 1,1,1-trifluoroethane (2 mol.%) and 1,1-dichloro-ethene (5 mol.%). Exposure of the fluorinated gallium oxide to 1,1,1-trichloroethane produces a colour change from the initial white material, through orange to red–black. This colour change is consistent with the build up of polyenes at the fluorinated gallium oxide surface.[1] No colour change was observed for the fluorinated indium(III) oxide on exposure to the chlorohydrocarbon, except for a deepening of the initial yellow hue of the material. Products identified in the F/In_2O_3 system are 1,1-dichloro-1-fluoroethane (12 mol.%), 1-chloro-1,1-difluoroethane (2 mol.%), 1,1,1-trifluoroethane (2 mol.%) and 1,1-dichloroethene (4 mol.%). Only the fluorinated gallium oxide performed β-scission of CH_3CCl_3 to give chlorotrifluoromethane (5 mol.%). Similar catalytic performance is observed for the fluorinated gallium oxide with 1,1-dichloroethene, such that both 1,1-dichloro-1-fluoroethane (11 mol.%) and 1-chloro-1,1-difluoroethane (2 mol.%) is formed along with the C_1 product chlorotrifluoromethane (5 mol.%). The majority of the fluorine originating from the fluorinated gallium oxide surface is contained in the $CClF_3$ fraction, which accounts for 38% of the exchanged fluorine. The formation of the reaction products CH_3CCl_2F and CH_3CClF_2 from CH_3CCl_3 in the presence of Lewis acid catalysts has been reported to proceed through an intermolecular dehydrochlorination step, followed by a hydrofluorination step, by way of the generation of carbocation intermediates at the halogen promoted surface.[21,22] It is proposed that this process occurs at a co-ordinatively unsaturated metal centre, where fluorine has replaced bridging lattice oxygen at the metal oxide surface. The extent of fluorination of the probe molecule is greater for the fluorinated indium(III) oxide where 27% of the exchanged fluorine is incorporated in CH_3CF_3 compared with 15% from the fluorinated gallium(III) oxide. Fluorinated indium(III) oxide did not display β-scission capability, whereas 38% and 48%, respectively, of fluorine originating from the gallium(III) oxide surface is found in the $CClF_3$ from CH_3CCl_3 and $CH_2=CCl_2$ substrates. The ability of fluorinated gallium oxide to induce β-scission of the carbon bond in C_2 precursor molecules is consistent with a strong Lewis acid character from the surface and, hence, these results show that the Pearson hardness[23] for F/Ga_2O_3 is greater than that of F/In_2O_3.

Increasing the thermodynamic stability of the probe molecule towards dehydrochlorination by reacting asym-tetra-chloroethane,[24] shifts the product distribution from halohydrocarbons to halocarbon compounds (Tables 1 and 2).

Table 1 Product distribution for the reaction of chlorocarbons and chlorohydrocarbons with fluorinated gallium(III) oxide

product (mol.%)	reagent							
	$CHCl_3$	CH_2Cl_2	CCl_4	$CCl_2=CCl_2$	CCl_2FCClF_2	CH_2ClCCl_3	$CH_2=CCl_2$	CH_3CCl_3
CH_2ClCF_3	2.5							
$CH_2ClCClF_2$	4	11		2				
CH_2FCF_3	4							
CCl_3F			14					
CCl_2F_2			2					
$CClF_3$				3	6		5.1	5.1
$CCl_2FCCl2F$				1				
CCl_3CF_3				2	7	15		
CH_3CClF_2		15					2	3
CH_3CF_3								2
$CH_2=CCl_2$								5
CH_2ClCCl_2F				5		1		
CCl_4				1				
$CHCl=CCl_2$				2				
$(CH_3)_3CH$		1						
$(CH_2Cl)_4C$	1	1						
$(CH_2Cl)_3CCl$	1	1		1				
$CHCl_2CCl_3$	1	2		2				
$CCl_2=CCl_2$			2					
$CHCl_2CHCl_2$	2			2				
CH_3CCl_2F		9					11.6	12

Table 2 Product distribution for the reaction of chlorocarbons and chlorohydrocarbons with fluorinated indium (III) oxide

product (mol.%)	reagent					
	$CHCl_3$	CCl_4	$CCl_2=CCl_2$	CCl_2FCClF_2	CH_2ClCCl_3	CH_3CCl_3
CCl_2FCClF_2		5	3		2	
CCl_3CF_3		6	5	4	5	
$CClF_3$	9	1	1			
$CH_2=CCl_2$	3					4
$CH_2ClCClF_2$			3			
CH_3CCl_2F				1		12
CH_3CClF_2						2
CH_2Cl_2	3					
CH_3CF_3						2

For the fluorinated gallium(III) oxide material, 98% of the total fluorine exchanged was found in the 1,1,1-chlorotrifluoroethane fraction. Fluorinated indium(III) oxide utilised all the exchangeable fluorine to give C_2 chlorofluorocarbons, namely a mixture of 1,1,2-trichlorofluoroethane (29%, 2 mol.%) and the thermodynamically stable isomer 1,1,1-trichlorotrifluoroethane (71%, 5 mol.%).[25] Similarly, tetrachloroethene gives a high ratio of chlorofluorocarbons as products. Reaction of C_2Cl_4 with fluorinated gallium oxide, results in 66% of the exchanged fluorine distributed between the CCl_3CF_3 and CCl_2FCClF_2 fractions, of which the β-scission product $CClF_3$ contains 33% of the exchanged fluorine. The reaction of tetrachloroethane with fluorinated indium(III) oxide, gives 90% of the products as C_2 chlorofluorocarbons, with 1,2,2-trichloro-2-fluoroethane (5 mol.%) and 1,2-dichloro-2,2-difluoroethane (2 mol.%) making up the fluorine balance (Table 1). Fluorinated indium(III) oxide exhibits β-scission capability towards the sp^2 hybridised carbon of the tetrachloroethene molecule. For the F/Ga_2O_3 reaction with C_2Cl_4, chlorohydrocarbon compounds identified by ^1H NMR and/or gas chromatographic mass spectroscopy (GCMS) are carbon tetrachloride (1 mol.%), 1,2,2-trichloroethene (2 mol %), pentachloroethane (2 mol.%) and 2-chloromethyl-1,3-dichloropropane ($\delta_H = 3.35$, 1.58; 1 mol.%). Pentachloroethane can be formed by the hydrochlorination of tetrachloroethene in the presence of Lewis acid sites.[1] The production of $(CH_2Cl)_3CCl$ however, suggests the role of radical species at the catalyst surface. The reaction of fluorinated indium(III) oxide with the tetrachloroethene results in 45% of the exchanged fluorine incorporated into the product CCl_3CF_3. Analysis of the exchanged fluorine content of CCl_2FCClF_2 is 29% to give a CCl_3CF_3/CCl_2FCClF_2 ratio of 1.7, the relative ratio of $k_{formation}$ for the isomers of trichlorotrifluoroethane at ambient temperatures for the catalyst system. The fluorine ratio of the isomers of trichlorotrifluoroethane for the fluorinated gallium oxide material is 1.8. These results are consistent with the same rates of forward and backward reactions operating in the isomerisation process for trichlorotrifluoroethane produced from the probe molecule C_2Cl_4. The relative ratio of fluorine in the $CClF_3/CCl_2FCClF_2$ fractions is 2.7 and 0.3 for F/Ga_2O_3 and F/In_2O_3, respectively. This result indicates the enhanced efficiency of the fluorinated gallium oxide to induce β-scission in both isomers of trichlorotrifluoroethane relative to fluorinated indium oxide. Using CCl_2FCClF_2 and CCl_3CF_3 as probe molecules confirms that β-scission of the carbon–carbon bond only occurs with F/Ga_2O_3 to yield $CClF_3$, with isomerisation of CCl_2FCClF_2 to CCl_3CF_3 (Tables 1 and 2). No β-scission of the chlorofluorocarbon occurs for F/In_2O_3.

The reactions of the C_1 probe molecules methylene chloride, chloroform and carbon tetrachloride are also presented in Tables 1 and 2. The reaction of CH_2Cl_2 with fluorinated gallium(III) oxide produces CH_3CCl_2F (9 mol.%), CH_3CClF_2 (15 mol.%) $CH_2ClCClF_2$ (11 mol.%) and CCl_2FCClF_2 (3 mol.%). Hydrocarbon and chlorohydrocarbon compounds identified are $(CH_3)_3CCl$ ($\delta_H = 1.58$; 1 mol.%), $(CH_3)_3CH$ ($\delta_H = 1.56$, 0.88; 1 mol.%), $(CH_2Cl)_4C$ ($\delta_H = 3.35$; 1 mol.%) and $CHCl_2CCl_3$ (2 mol.%). The presence of the symmetrical butyl complexes is consistent with the presence of radical species during the reaction. The reaction of trichloromethane with fluorinated indium(III) oxide gives trichlorofluoromethane (9 mol.%), and dichloroethene (3 mol.%), whereas the fluorinated gallium(III) oxide material gives $CClF_3$ (2 mol.%), $CH_2ClCClF_2$ (4 mol.%), CH_2ClCF_3 (2.5 mol.%) and CH_2CCl_2 (4 mol.%). The chlorohydrocarbon compounds identified are sym-tetrachloroethane, asym-tetrachloroethane, $(CH_2Cl)_4C$ (1 mol.%), $(CH_3)_3CCl$ (1 mol.%) and pentachloroethane (0.5 mol.%). The reactivities of the fluorinated gallium and indium oxide surfaces are reversed for the reaction of CCl_4, which for fluorinated gallium(III) oxide, gives only C_1 products, CCl_2F_2 (2 mol.%) and CCl_3F (14 mol.%),

whereas fluorinated indium(III) oxide yields $CClF_3$ (0.5 mol.%) and the C_2 compounds CCl_2FCClF_2 (5 mol.%) and CCl_3CF_3 (6 mol.%).

Discussion

The ability of chloroethane probe molecules to undergo intramolecular dehydrochlorination has been shown to be a function of the degree of chlorine substitution on the β-carbon, such that $CH_3CHCl_2 < CH_2ClCHCl_2 < CH_3Cl_3$.[24] Studies have shown that this intramolecular dehydrochlorination mechanism is consistent with the formation of a carbocation intermediate at the catalyst surface.[21,22,26] 1,1,1-Trichloroethane is thermodynamically unstable with respect to dissociation into dichloroethene and gaseous hydrogen chloride.[24] The room temperature equilibrium constant (K_c) for the reaction is 2×10^{-3} mol l^{-1} equivalent to ca. 1.5% dissociation. In the presence of fluorinated or chlorinated γ-alumina, magnetite, and cobalt(II,III) oxide respectively, 1,1,1-trichloroethane readily undergoes dehydrochlorination with the subsequent formation of polyene species at the catalyst surface.[4] The ability of β-gallium oxide to induce low temperature dehydrochlorination, confirms the presence of strong Lewis acid sites at the halogenated surface. The change in the colour of the catalyst from white through to black–purple on exposure of gaseous 1,1,1-trichloroethane is consistent with the build up of polyene moieties at the surface.[1] Notably the formation of polyenic species at the catalyst surface was not the case for the indium(III) oxide, even though the extent of the distribution of fluorine containing volatile materials is comparable (Tables 1 and 2). The fluorinated gallium(III) oxide displays an ability to induce β-scission to C_1 compounds for 1,1,1-trichloroethane, whereas for the fluorinated indium(III) oxide only dehydrochlorination/hydrofluorination products are observed. β-Scission of C_2 compounds at the fluorinated gallium(III) oxide is a measure of the Pearson hardness of the surface and shows that the relative acidity of F/Ga_2O_3 is greater than that of F/In_2O_3.

Increasing the thermodynamic stability of the probe molecule towards the dehydrochlorination reaction by probing the freshly prepared catalyst fluorinated gallium and indium oxide surfaces with asym-tetrachloroethane, highlights the differences in the reactivity of these materials. The fluorinated gallium oxide material gives the Cl-for-F exchange compound 1,2-dichloro-2,2-difluoroethane and the chlorofluorocarbon molecule 1,1,1-trichlorotrifluoroethane. Conversely, fluorinated indium oxide produced only chlorofluorocarbons, namely, 1,1,2-trichlorotrifluoroethane, and 1,1,1-trichlorofluoroethane. The formation of 1,2-dichloro-2,2 difluoroethane is consistent with the catalyst inducing a dehydrochlorination/hydrofluorination mechanism in the adsorbed compound. The presence of chlorofluorocarbons in the product mixture evidences an exchange mechanism that removes hydrogen and inserts the halogen into the molecule. This halogen exchange mechanism is observed by both fluorinated gallium and indium oxides, respectively. For CH_2ClCCl_3 the thermodynamic ratio of the CCl_3CF_3/CCl_2FCClF_2 of 2.5 is greater than the values of 1.7 and 1.8 observed for the tetrachloroethene system, and double that of 1.2 observed for the carbon tetrachloride system. The ratios of the isomers of CCl_3CF_3 are proportional to the rates of formation of the isomers of trichlorotrifluoroethane from the forward and reversed isomerisation reactions. Based on these results, reactivities for the formation of $C_2Cl_3F_3$ isomers from CH_2ClCCl_3 are a factor of two greater than that for C_2Cl_4 and five times greater than that for CCl_4. Given that the heats of adsorption are the same for the adsorbed states of the chlorofluorocarbon isomers, these results suggest that the CCl_2FCClF_2 or CCl_3CF_3 precursor species are formed directly from the probe molecule

rather than an equilibrium generated from an isomerisation mechanism of either trichlorotrifluoroethane compound.

The reaction of tetrachloroethene with fluorinated gallium oxide gives products which are again consistent with radical species being generated at the catalyst surface. The volatile chlorohydrocarbons produced from the reaction of C_2Cl_4 are 1,1,2-trichloroethene, pentachloroethane, and 2-chloromethyl-1,3-dichloropropane $[(CH_2Cl)_3CCl]$. Statistical treatment shows that the probability is infinitely low for three discreet identical radical species to focus at an equilibrium node, to combine with, or abstract a halogen or proton from the halomethane substrate molecule during the formation of $(CH_2Cl)_3Cl$. The presence of 2,2-dimethylpropane and analogues (2-chloro-2-methylpropane, 1,3-dichloro-2,2-chloromethylpropane) in the reaction products from dichloromethane also supports a radical propagation mechanism through the formation of the chloromethane radical and carbon tetrachloride.
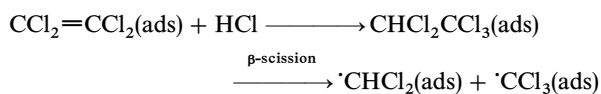
In order to understand the generation of radical species at the catalyst surface it is necessary to consider the chemical environment where there is deposition of organic material at the Lewis acid surface. The exposure of the chlorohydrocarbon to fluorinated gallium oxide builds up polyenic species at the catalyst surface through the polymerisation of alkenic material generated by the dehydrochlorination of adsorbed chlorohydrocarbons. *In situ* dehydrochlorination of the polymeric material generates sp^2 hybridised moiety from the saturated organic material.[5,24] Polar conditions generated at the catalyst surface, which include the polyenic overlayer, can result in an equilibrium being established between the solvated alkenes and radical character:
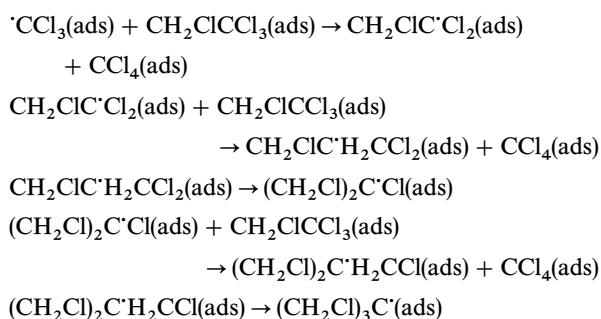
$$CH_2=CX_2(ads) \rightleftharpoons \,^\cdot CH_2—CX_2(ads)$$
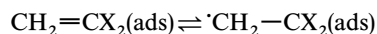
The presence of β-scission products evidences the strong polarisation conditions at the catalyst surface, which result in the bond fission of C_2 probe molecules. Formation of radical species from C_1 precursors generated by heterolytic fission of the sp^3 bond during bond metathesis occurs in conjunction with a modest increase in bond length of the substrate molecule.[27] Abstraction of a substrate atom can also be induced by free ions (*e.g.*, Cl$^-$), where polarisation of the electron cloud induces C_{3v} symmetry to hybridise to D_3 symmetry which lowers the potential energy barrier and so induces the metathesis reaction.[27]

A reaction mechanism which accounts for the radical chain propagation mechanism is proposed for C_2Cl_4 or CH_2ClCCl_3.
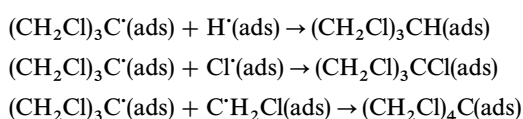
Initiation

$$CCl_2=CCl_2(ads) + HCl \xrightarrow{\hspace{3cm}} CHCl_2CCl_3(ads)$$

$$\xrightarrow{\text{β-scission}} \,^\cdot CHCl_2(ads) + \,^\cdot CCl_3(ads)$$

Propagation

$$^\cdot CCl_3(ads) + CH_2ClCCl_3(ads) \rightarrow CH_2ClC^\cdot Cl_2(ads) + CCl_4(ads)$$

$$CH_2ClC^\cdot Cl_2(ads) + CH_2ClCCl_3(ads)$$
$$\rightarrow CH_2ClC^\cdot H_2CCl_2(ads) + CCl_4(ads)$$

$$CH_2ClC^\cdot H_2CCl_2(ads) \rightarrow (CH_2Cl)_2C^\cdot Cl(ads)$$

$$(CH_2Cl)_2C^\cdot Cl(ads) + CH_2ClCCl_3(ads)$$
$$\rightarrow (CH_2Cl)_2C^\cdot H_2CCl(ads) + CCl_4(ads)$$

$$(CH_2Cl)_2C^\cdot H_2CCl(ads) \rightarrow (CH_2Cl)_3C^\cdot(ads)$$

Termination

$$(CH_2Cl)_3C^\cdot(ads) + H^\cdot(ads) \rightarrow (CH_2Cl)_3CH(ads)$$

$$(CH_2Cl)_3C^\cdot(ads) + Cl^\cdot(ads) \rightarrow (CH_2Cl)_3CCl(ads)$$

$$(CH_2Cl)_3C^\cdot(ads) + C^\cdot H_2Cl(ads) \rightarrow (CH_2Cl)_4C(ads)$$

The above reaction scheme proposes the formation of the $^\cdot CH_2Cl$ radical intermediate and the sequential radical propagation steps in conjunction with a chlorine re-arrangement.
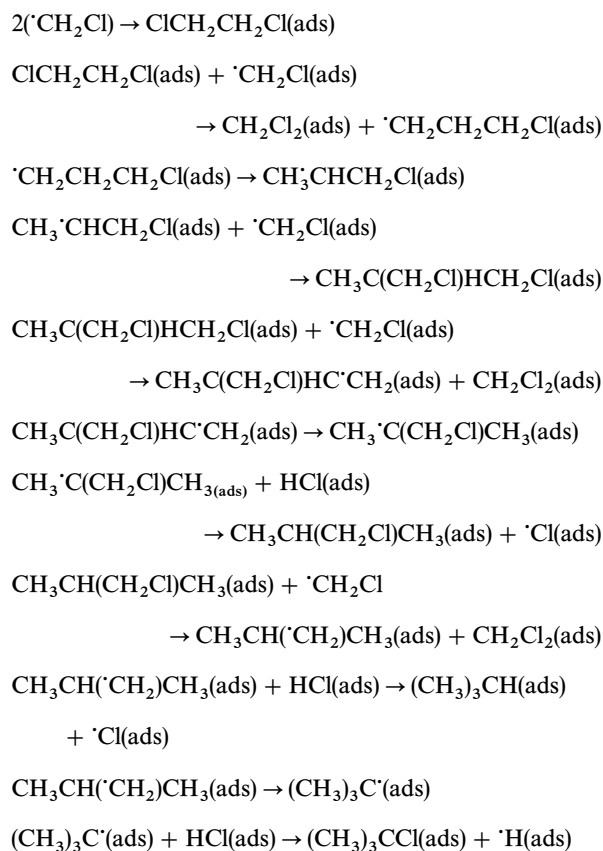
The product distribution from the reaction of tetrachloroethene included 1,2,2-trichloro-2-fluoroethane, 1,2-dichloro-2,2-difluoroethane, 1,2-difluorotetrachloroethane, 1,1,1-trichlorotrifluoroethane and chlorotrifluoromethane (Table 1). β-Scission of CH_2ClCCl_2F gives $^\cdot CH_2Cl$ and $^\cdot CCl_2F$, whereas CH_2ClClF_2 gives $^\cdot CH_2Cl$ and $^\cdot CClF_2$. Radical recombination of the fluorine containing species is consistent with the production of 1,2,2-trichlorotrifluoroethane and the subsequent isomerisation to 1,1,1-trichlorotrifluoroethane.[4] Similar compounds are obtained from the reactions of chloroform and methylene chloride with fluorinated gallium oxide. For the reaction of methylene chloride with fluorinated gallium oxide, compounds identified included gaseous hydrogen chloride, pentachloroethane, 2-chloro-2-methylpropane $[(CH_3)_3CCl]$, 1,1-dimethylethane $[(CH_3)_3CH]$, and 1,3-dichloro-2,2 dichloromethylpropane $[(CH_2Cl)_4C]$. The reaction of chloroform gives sym-tetrachloroethane, asym-tetrachloroethane, 1,3-dichloro-2,2-dichloromethylpropane, 2-chloro-2-methylpropane.

The reaction scheme below proposes the formation of the $^\cdot CH_2Cl$ radical intermediate and the sequential radical propagation steps by metathetic abstraction, in conjunction with a 1,2-chlorine migration as follows.
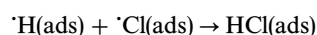
Initiation

$$CH_2Cl_2(ads) \rightarrow \,^\cdot CH_2Cl(ads) + \,^\cdot Cl(ads)$$

Propagation

$$2(^\cdot CH_2Cl) \rightarrow ClCH_2CH_2Cl(ads)$$

$$ClCH_2CH_2Cl(ads) + \,^\cdot CH_2Cl(ads)$$
$$\rightarrow CH_2Cl_2(ads) + \,^\cdot CH_2CH_2CH_2Cl(ads)$$

$$^\cdot CH_2CH_2CH_2Cl(ads) \rightarrow CH_3^\cdot CHCH_2Cl(ads)$$

$$CH_3^\cdot CHCH_2Cl(ads) + \,^\cdot CH_2Cl(ads)$$
$$\rightarrow CH_3C(CH_2Cl)HCH_2Cl(ads)$$

$$CH_3C(CH_2Cl)HCH_2Cl(ads) + \,^\cdot CH_2Cl(ads)$$
$$\rightarrow CH_3C(CH_2Cl)HC^\cdot CH_2(ads) + CH_2Cl_2(ads)$$

$$CH_3C(CH_2Cl)HC^\cdot CH_2(ads) \rightarrow CH_3^\cdot C(CH_2Cl)CH_3(ads)$$

$$CH_3^\cdot C(CH_2Cl)CH_{3(ads)} + HCl(ads)$$
$$\rightarrow CH_3CH(CH_2Cl)CH_3(ads) + \,^\cdot Cl(ads)$$

$$CH_3CH(CH_2Cl)CH_3(ads) + \,^\cdot CH_2Cl$$
$$\rightarrow CH_3CH(^\cdot CH_2)CH_3(ads) + CH_2Cl_2(ads)$$

$$CH_3CH(^\cdot CH_2)CH_3(ads) + HCl(ads) \rightarrow (CH_3)_3CH(ads)$$
$$+ \,^\cdot Cl(ads)$$

$$CH_3CH(^\cdot CH_2)CH_3(ads) \rightarrow (CH_3)_3C^\cdot(ads)$$

$$(CH_3)_3C^\cdot(ads) + HCl(ads) \rightarrow (CH_3)_3CCl(ads) + \,^\cdot H(ads)$$

Termination

$$^\cdot H(ads) + \,^\cdot Cl(ads) \rightarrow HCl(ads)$$

The above proposed mechanism supports a 1,2-migration of hydrogen and hence supports an intramolecular bridged radical moiety. Interestingly, no fluorine containing analogue

of 2,2-dimethylpropane is observed in the reaction products and is consistent with a radical chain propagation mechanism.

Conclusions

Product distribution of the reactions of fluorinated gallium(III) oxide with a range of C_1 and C_2 chlorohydrocarbons and chlorocarbon probe molecules, confirms the strong Lewis acid nature of the material. β-Scission of C_2 compounds are also found for reactions of fluorinated gallium(III) oxide. The formation of symmetrical butyl complexes and derivatives from C_2 and C_1 precursor molecules is consistent with the formation of radical species at the catalyst surface. The Lewis acid character of fluorinated indium(III) oxide exhibits lower reactivity towards the probe molecules. The chemistry exhibited by these materials is not solely limited to that of ionogenic mechanisms.

References

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