Low temperature preparation of fluoroalkanes from a mixture of carbon tetrachloride, dichloromethane and anhydrous hydrogen fluoride using a fluorinated γ-alumina supported iron(II, III)/cobalt(II, III) oxide catalyst

James Thomson

Department of Chemistry, University of Dundee, Dundee DD1 4HN, Scotland, UK

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1,1,1,2-tetrafluoroethane has been prepared at 473 K under static conditions, from a feedstock of carbon tetrachloride, dichloromethane and anhydrous hydrogen fluoride using a γ-alumina supported fluorinated Co(II, III)$_{85}$Fe(II, III)$_{15}$O$_x$ catalyst. Conversion to hydrofluoroalkanes was ca. 58% efficiency as quantified by liquid phase ^{19}F NMR analysis.

Keywords: 1,1,1,2-tetrafluoroethane; hydrofluorination; cobalt(II, III) oxide; iron(II, III) cobalt(II, III) mixed oxide catalyst

1. Introduction

The preparation of hydrofluoroalkanes has received a great deal of attention since this class of compound has been selected by industry to replace chlorofluorocarbons in a wide variety of applications from refrigerants and foam blowers to aerosol propellant. The preparation of the chlorofluorocarbon replacement hydrofluoroalkane 1,1,1,2-tetrafluoroethane has received particular attention, as this molecule has been identified as the primary replacement compound to be used in refrigeration manufacture replacing the compound dichlorodifluoromethane in this role. However, the route to 1,1,1,2-tetrafluoroethane utilised by the majority of CFC producers requires the continued preparation of the chlorofluorocarbon intermediate 1,1-dichlorotetrafluoroethane which subsequently undergoes the hydrogenolysis reaction on a carbon or an aluminium(III) fluoride supported palladium catalyst to yield 1,1,1,2-tetrafluoroethane [1–3]. Hence the preparative route involves the continued preparation of 1,1-dichlorotetrafluoroethane from hexachloroethane and anhydrous hydrogen fluoride using a fluorinated chromia catalyst at ca. 700 K [4], followed by the hydrogenolysis step to 1,1,1,2-tetrafluoroethane.

In our search for an environmentally benign catalyst to prepare chlorofluorocarbons thereby eliminating the necessity for the use of chromia in the preparation of 1,1,1,2-tetrafluoroethane, we found that fluorinated cobalt(II, III) oxide produced C$_2$ chlorofluorocarbons from C$_1$ substrate materials, and that the catalytic reaction was consistent with the formation of radical species generated from the substrate compound at the fluorinated oxide surface [5]. Studies of the fluorinated iron(II, III) oxide system towards halogen exchange indicated that radical stability was less efficient than that achieved by the fluorinated cobalt(II, III) oxide material, owing to reduction of the Fe(III) environments by a radical species to Fe(II) [5]. Hence the presence of Fe(II, III) oxide induced "a radical quenching effect" and was therefore synthesised into the catalytic material to influence the radical intermediates generated from CH$_2$Cl$_2$. We considered the feasibility of an iron/cobalt catalytic system to generate a mixture of radical species from a feedstock of carbon tetrafluoride and dichloromethane, the radical species so generated able to subsequently undergo a halogen exchange (F-for-Cl) reaction. Such a system would have the ability to produce C$_2$ hydrofluoroalkanes from C$_1$ halocarbon substrates, and hence a one-step, low-temperature, route to the production of hydrofluoroalkanes.

Therefore, the objective of the present paper is to investigate the potential use of fluorinated iron(II, III) cobalt(II, III) mixed oxide to produce 1,1,1,2-tetrafluoroethane from a mixture of CCl$_4$, CH$_2$Cl$_2$ and anhydrous hydrogen fluoride.

2. Experimental

Degussa C γ-alumina (5 g, BET surface area 110 m^2 g^{-1}) was co-impregnated with 200 cm^3 of 0.02 M cobalt(II) nitrate hexahydrate solution (Aldrich Chemicals) and 100 cm^3 of 7.4×10^{-3} M iron(II) nitrate nonahydrate solution (Aldrich Chemicals) and refluxed with stirring at 353 K for 3 h. The solution was then evaporated to dryness and the "cake" transferred to a flow reactor and reacted with di-oxygen (flowrate 50 cm^{-3} min^{-1}) at 673 K. The catalyst charge (0.5 g) was transferred to a conditioned stainless steel bomb and heated to 523 K in vacuo over a 4 h period. The catalyst was finally reacted with sulphur tetrafluoride at room temperature (14 mmol, Air Products) to give a catalyst fluorine content of 1.7 mmol (g catalyst)$^{-1}$, as analysed by CCl_4 titration under pulse flow conditions at 323 K. Reagent CCl_4 (Aldrich Chemical Co., 3 mmol) and CH_2Cl_2 (Aldrich Chemical Co., 1 mmol) were degassed in vacuo by three pump–freeze–thaw cycles and condensed into the reaction vessel at 77 K. Samples of the prefluorinated $Co_{85}Fe_{15}O_x/\gamma$-Al_2O_3 material were reacted by the sequential addition of a mixture of CCl_4/CH_2Cl_2/HF (3 : 1 : 14) The system was warmed to room temperature and allowed to react over a 2 h period. The volatile material from the reaction was condensed in vacuo onto activated sodium fluoride in deuterochloroform (Aldrich Chemical Co., 0.75 ml) at 77 K. After a period of 20 min, the volatile material was condensed into an NMR side-arm and analysed using liquid phase ^{19}F and ^{1}H NMR (Bruker AM300). X-ray diffraction (XRD) experiments were performed using a Philips PW1010 X-ray generator fitted with a PW 2213/20 1.5 kW copper tube running at 40 kV.

3. Results and discussion

X-ray diffraction analysis of the freshly calcined material gives 2θ bands at 18.85, 28.92, 31.08, 36.65, 44.8, 45.52, 55.55, 59.12, 65.12 and 66.9 which correlate to δ (Å) of 4.71, 3.09, 2.88, 2.45, 2.02, 1.99, 1.65, 1.56, 1.43, and 1.40 respectively. The δ (Å) measurements of 3.09, 1.99 and 1.40 correspond to the γ-Al_2O_3 phase, with the residual reflections consistent with that of a cubic Co_3O_4 or Fe_3O_4 structure and confirms that the calcination process [6], under the conditions used, generates the spinel and inverse spinel structures of the cobalt(II, III) oxide and iron(II, III)oxide respectively. The data was not able to indicate if the supported oxides were homogeneous.

The product distribution for the static in vacuo reactions of carbon tetrachloride, dichloromethane, and a substrate mixture of carbon tetrachloride/dichloromethane (ratio 3 : 1) respectively, with fluorinated Co(II, III)/Fe(II, III) oxide are presented in table 1. The results show that the presence of CCl_4 generates substantial molar fractions of trichlorofluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12) across the range of reaction temperatures. The reactions are performed under static conditions and by a warm up from the condensed substrate from 77 K. Hence these results are consistent with the fluorination of carbon tetrachloride from the liquid phase during the thermal window between melting and boiling of the CCl_4 fraction. The reactions of methylene chloride and a mixture of methylene chloride/carbon tetrachloride generate C_2 complexes are consistent with our previous findings [2]. The results show the production of 1,1,1,2-tetrafluoroethane and pentafluoroethane (6.6 and 5.4 mol%). The substrate CH_2Cl_2 readily generates a higher proportion of C_2 halocarbons relative to the substrate carbon tetrachloride [3]. The fraction "others" comprising of 1,1-difluoroethane (11.6 mol%), 1,1,2-trichlorotrifluoroethane (28.4 mol%). The feedstock combination of CCl_4/ CH_2Cl_2/ HF produced quantities of 1,1,1,2-tetrafluoroethane as evidenced by the doublet ^{1}H NMR peak at $\delta_H = 0.83$ ppm and the ^{19}F peak at $\delta_F = -78.38$ ppm and a $J_{F-H} = 16$ Hz, pentafluoroethane (doublet at $\delta_F = -110.31$ ppm and $J_{F-H} = 51$ Hz) and 1-chloro-1,2,2-trifluoroethane ($\delta_F = -156$ ppm and $J_{H-F} = 48$ Hz). Fluorine conversion in the hydrofluoroalkane fraction was ca. 58% with 22.1 mol% of C_2 hydrofluoroalkanes being produced. Of particular note was the presence of a large singlet ^{1}H peak at $\delta_H = 1.5$ ppm, of trimethylchloromethane ($(CH_3)_3CCl$) which supports the formation of radical intermediate species during the reaction.

Hence the $Co_85Fe_{15}O_x/\gamma$-Al_2O_3 system has been shown to be a "one pot no-chromia" route to the preparation of hydrofluoroalkanes.

Table 1

^{19}F product distribution from the reaction of CCl_4/CH_2Cl_2/HF at 473 K on fluorinated γ-Al_2O_3 supported $Co_{85}Fe_{15}O_x$

	Fluorine distribution (mol%)					
	CCl_3F	CCl_2F_2	$CF_2HCHClF$	CH_2FCF_3	CHF_2CF_3	others
CCl_4 feedstock only	35.6	14.4				50.2
CH_2CCl_2 feedstock only	5.3	6.1		5.4	6.6	82.0
CCl_4/CH_2Cl_2/HF						
catalytic run 1	41.8	19.0	12.3	1.0	9.1	16.8
2	40.7	19.4	12.0	1.1	9.0	17.8
3	41.3	20.5	12.0	0.8	9.0	16.4
4	40.8	18.4	12.0	1.0	8.9	18.9
5	41.2	19.1	12.4	0.8	7.8	18.7

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References

[1] J.I. Darragh, UK Patent 1578933 (1980).

[2] C.S. Keller and V. Mallenkarjuna, US Patent 4873381 (1989).

[3] J. Thomson, UK Patent Appl. 9306334.5 (1993); 9404802.2 (1994); Int. Patent Appl. GB 94/00477 (1994).

[4] A. McCulloch, L. Rowley, J. Thomson, G. Webb and J.M. Winfield, Appl. Catal. (1991) 79, 89.

[5] J. Thomson, J. Chem. Soc. Faraday Trans. 90 (1994) 3585.

[6] Powder Diffraction File Search Manual, JCPDS, Int. Centre for Diffraction Data, US (1977).