Zinc promoted alumina catalysts for the fluorination of chlorofluorocarbons

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ABSTRACT

A range of catalysts consisting of zinc impregnated γ-Al$_2$O$_3$ has been examined for the fluorination of chlorofluorocarbons. Addition of zinc to γ-Al$_2$O$_3$ promotes steady state fluorination of CF$_2$ClCFCl$_2$ (CFC-113) to 1,1,1,2-tetrafluoro-2,2-dichloroethane (CFC-114a). Zinc promotion of fluorination activity was maximised at 6.5 wt%. Temperature programmed reaction (TPR) studies on pre-fluorided catalysts show that CCl$_4$ is fluorinated by a sequential mechanism, with CCl$_3$F a primary product and CCl$_2$F$_2$ a secondary product. The addition of zinc to γ-Al$_2$O$_3$ resulted in a low temperature feature in the TPR profile, and further analysis shows that there is a strong correlation between catalyst activity for CFC-113 fluorination and the concentration of fluorine associated with this low temperature feature. As the site population of the low temperature feature increases the apparent activation energy for the CFC-113 fluorination process decreases. Higher temperature HF pre-treatment resulted in a significant reduction of the population of this low temperature site compared to the standard conditions without pre-treatment, indicating that active fluorine consists of labile surface bonded H-F, rather than a metal fluoride such as AlF$_3$ or ZnF$_2$. Based on experiments investigating highly dispersed zinc on an activated carbon support, zinc adjacent to an Al^{3+} ion is required for fluorination, since this allows adsorption of active HF in close proximity to a Lewis acid site, where the CFC can adsorb.

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1. Introduction

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) were developed for applications in refrigeration and air conditioning, where their thermodynamic properties coupled with low flammability make them ideal for use in heat exchangers. In the 1970s the link between atmospheric chlorofluorocarbons and the destruction of stratospheric ozone was established [1]. Subsequently, the magnitude of stratospheric ozone depletion was appreciated, leading to increased political pressure to restrict the use and emission of CFCs. As a consequence, in 1984, under the auspices of the United Nations, the Montreal protocol was agreed. This was the first international treaty relating to the protection of the environment. In 1987 the Montreal protocol finally gained commitment from governments around the world to reduce the production of CFCs to 50% of the 1986 levels by 1999. This was followed by the London amendment in 1990, which agreed the complete phase out of CFC production in developed countries by 2000,

and by 2010 in developing countries. In 2007 a further adjustment to these agreements accelerated the phasing out of HCFCs emitted to the atmosphere, with production and emission caps in 2013. Since 2013, monitoring has confirmed a stabilisation of the emission levels of HCFCs [2].

Against the background of environmental concerns, it became imperative to develop alternatives to CFCs with low ozone depletion potentials (ODP). Fluorine containing organic compounds emerged as the best candidates, combining the appropriate boiling points, low toxicity and non-flammability demanded by users in a wide variety of applications with zero ODPs. For example, 1,1,1,2-tetrafluoroethane (HFC-134a) is now used as a refrigerant, foaming agent and medical propellant. It has also been considered as a possible electrolyte material for a new generation of supercapacitors [3]. The wide spread availability of the compound for these applications has also led to the investigation of HFC-134a as a chemical feedstock in pharmaceutical production [4].

Despite negligible ODP, HFC-134a has recently been banned in automobile air conditioning units, due to its high global warming potential (GWP = 1300). Consequently, the environmental impact of compounds such as HFC-134a are still a concern and emissions of HFCs in general are targeted for significant reduction moving forward from the 1998 Kyoto Protocol. A new generation of

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fluorinated olefins are now being developed to supersede the HFCs. One example is 2,3,3,3-tetrafluorpropene (HFO-1234yf) which has similar thermodynamic properties to HFC-134a and a zero ODP but also GWP of only 4 [5].

Both HFC and HFO compounds can be conveniently produced through the fluorination of CFCs with suitable catalysts. HFC-134a can be obtained by the successive fluorination of trichloroethene with HF over trivalent metal fluorides or oxides as catalysts [6]. Vapour phase catalytic fluorination using anhydrous hydrogen fluoride over fluorided catalysts is a widely adopted route for the industrial scale production of chlorofluoroalkanes, and is also a route to HFO compounds [7]. A number of studies have reported the use of fluorided chromia as a catalyst for the fluorination of CFCs. Work on the mechanistic aspects of this process have included radioisotope labelling experiments, which showed that ^{18}F from chromia pre-fluorided with $H^{18}F$ appears in the fluorinated products when the reaction is carried out at elevated temperatures (973 °C) [8]. Catalysts impregnated with zinc have also been found to be superior fluorination catalysts in comparison with their non-doped counterparts [9]. However, the use of chromia as an industrial material has disadvantages for the treatment and disposal of the waste catalysts.

In the present study the fluorination of chloro-alkanes over zinc supported on γ-Al_2O_3 has been investigated. Initial studies have examined the steady state fluorination activity for the fluorination of $CF_2ClCFCl_2$ (CFC-113). Whilst, in order to probe the catalytic reactivity the reaction of CCl_4 on pre-fluorided Zn/γ-Al_2O_3 in the absence of gas phase HF was also examined using a temperature programmed reaction (TPR) approach. Even though conversion of CCl_4 is the simplest example of a fluorination reaction, the mechanism for this chlorocarbon fluorination has still not been precisely defined and our experiments were designed to identify key features of the catalyst required for activity. We also show that the low temperature activity for fluorination of CCl_4 is a good predictor for steady state fluorination of CFC-113, suggesting that our results give a general insight into the fluorination of CFC compounds to produce fluorinated alternatives.

2. Experimental

2.1. Catalyst preparation

A series of catalysts with varying zinc loadings, ranging from 0 to 12 wt%, on γ-Al_2O_3 were prepared by wet impregnation using aqueous zinc chloride (12.58 g in 50 cm^3 deionised water). The required amount of zinc chloride solution was added to pre-weighed γ-Al_2O_3 (8–10 g, Harshaw Al-3996R, surface area = 200 $m^2\,g^{-1}$). The mixture was stirred to ensure thorough wetting of the solid by the solution, heated on a hot plate to remove excess water and calcined in static air at 350 °C for 15 h. The resultant solid was pelleted and sieved, to a particle size of 0.5–1.4 mm.

Catalysts consisting of zinc supported on carbon (Zn/C (2 and 10 wt%), and ZnO were also prepared. The Zn/C catalyst was prepared by impregnating Norit activated carbon (Norit-RBAA3, surface area = 2000 $m^2\,g^{-1}$) with a solution of ZnF_2. The resulting material was mixed, dried and calcined using the same procedure described for the production of alumina supported catalysts. Zinc oxide (Aldrich, surface area = 5 $m^2\,g^{-1}$) was used as supplied and was pelleted to a uniform particle size range of 0.5–1.4 mm before testing.

2.2. Catalyst characterisation

Catalysts were characterised by powder X-ray diffraction (XRD) using an Enraf Nonius PSD120 diffractometer with a monochro-

matic CuK_{a1} source operated at 40 keV and 30 mA. Surface areas were determined by multi point N_2 adsorption at −196 °C, and data was treated in accordance with the BET method.

X-ray photoelectron spectroscopy (XPS) was carried out using a Surface Science Interface instrument with two X-ray sources. The first was a monochromatic aluminium source (M-Probe), and the second was a dual magnesium/aluminium non-monochromatic source. Catalyst samples were transferred into the spectrometer *via* a nitrogen-purged glove box. Samples were placed onto stubs using double-sided adhesive tape. Fine mesh iron grids were placed over the samples and an electron flood gun (0.5–1.0 eV) was used during analysis in order to improve compensation for charging. Analysis was largely carried out using the M-Probe source, operated at 10 kV and 12.5 mA, with a residual pressure in the analysis chamber of 5×10^{-9} torr. Binding energies were referenced with respect to adventitious carbon.

2.3. Catalyst testing

Micro-reactor apparatus: The reactor was constructed from nickel/copper alloy (Monel) and polytetrafluoroethene (PTFE) tubing. It was used to dry and fluorinate catalyst precursors *in situ*, as well as being used to examine catalysts under continuous flow conditions at atmospheric pressure. Further, it was also used to contain the catalyst during temperature programmed reaction studies. The catalytic reactor consisted of a 1/4-inch Monel U-tube, inside one end of which the catalyst was supported on a Monel gauze. A brass heat sink was clamped to the reactor tube around the catalyst. The heat sink jacket was fitted with thermocouples and engineered to allow accurate controlled heating, and quick cooling via the incorporation of a liquid nitrogen gas-cooling unit. The reactor tube was situated within an oven, allowing accurate temperature control (±2 °C). Further details of the experimental set up is included in Supplementary Data, Section S1 including schematics of the experimental equipment used (Figs. S1 and S2).

The reactants were delivered using saturators that were housed in an insulated thermostated bath with the temperature maintained by means of a liquid nitrogen chiller unit fitted with a temperature controller, ensuring that a high degree of thermal stability was maintained. Nitrogen flow rates through the saturators were controlled and monitored using thermal mass flow controllers.

Gas analysis was performed on-line using a Chrompak CP9000 gas chromatograph, fitted with a flame ionisation detector. The gas chromatograph contained a system of two Poraplot Q columns that were operated in series. These were separated by a 10-port valve, allowing isolation of the individual columns. This made it possible to analyse CCl_4 using the first column whilst CCl_3F and CCl_2F_2 were eluted from the second column. This system is well suited to short analysis times, allowing online injections to be taken at two-minute intervals. The apparatus was calibrated daily using a series of reactant and product standards.

2.3.1. Catalyst fluorination

Prior to determining the steady state catalyst activity and temperature programmed reaction studies the catalyst sample (5 g) was pre-treated with HF. N_2 (100 $cm^3\,min^{-1}$) was passed over the catalyst bed and the oven was heated to 300 °C for 30 min. This drying period served to remove water and weakly bound hydroxyl groups from the catalyst surface. Catalysts were exposed to HF/N_2 for 15 h at 300 °C. A consistent HF mass flow was established by passing N_2 through a thermostatically controlled Monel saturator containing HF, maintained at 5 °C ± 2 °C. The N_2 flow rate was set to approximately 5 $cm^3\,min^{-1}$ and then adjusted to give an HF mass flow of 0.025 g min^{-1}, determined by the time required to neutralise known aliquots of a basic solution at the reactor