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Catalytic fluorination of 1,1,1-trifluoro-2-chloro-ethane in the presence of oxygen over chromium based catalyst doped or not by zinc supported over partially fluorinated alumina

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ABSTRACT

The addition of zinc in low amount to chromium based catalyst supported over partially fluorinated alumina has a positive effect for the fluorination reaction of CF_3CH_2Cl in the presence of dioxygen in order to prevent the catalyst deactivation. However, under these operating conditions, the Deacon reaction by reaction with HCl produced by Cl/F exchanges could be involved. The formation of various by-products was observed corresponding to the addition of HCl or Cl_2 into halogenated double bonds.

1. Introduction

Chromium oxide based catalysts are commonly involved in the preparation of CFCs substitutes. For example, chromium oxides modified or not by another metal such as zinc, nickel or magnesium were used for the gas phase fluorination of CF_3CH_2Cl to CF_3CH_2F by Cl/F exchange [1–8] in the presence of hydrogen fluoride as fluorinating agent. On the other hand, several studies [9–16] showed that the presence of other elements (zinc, nickel, magnesium) could improve the catalytic properties of the chromium sites involved in Cl/F exchange by increasing the total activity and also by decreasing the contribution of secondary reactions. Winfield and co-workers [10] reported that zinc added in small amount to chromium increased its activity for the transformation of CF_3CH_2Cl. The presence of zinc could modify HF adsorption which became weaker. The consequence was lower apparent activation energy. Previous work [16] showed that the best promoting effect was observed, for the transformation of CF_3CH_2Cl, for an Zn/(Zn+Cr) atomic ratio of 0.15 and with a low (Zn+Cr) content of 2 wt%. This corresponds to a better dispersion of the different elements on the surface. On the other hand, previous studies [17–21] showed that to be active, the chromium species must be reversibly oxidizible which corresponds also to the presence of Cr^{VI} species in the initial material. The catalytic properties depend also on the composition of the catalyst and mainly on the amount of oxygen in the material. For example, an excess of oxygen in the starting chromium oxide is necessary to obtain the highest intrinsic catalytic activity for the transformation of CF_3CH_2Cl. Indeed the presence of oxygen in excess maintains HF labile (corresponding to chemisorbed HF on the catalyst surface which could be involved in Cl/F exchanges) and prevents the irreversible fluorination of the catalyst. A very low catalytic activity was reported over a CrF_3 catalyst [18]. Moreover, the presence of oxygen in continuous or discontinuous regime (in the very low amount 2 wt%) [2], prevent the catalyst deactivation by maintaining the catalyst surface. However, in this case, the Deacon reaction could be observed by reaction between HCl and O_2 (Eq. (3)).

This paper deals with the transformation of CF_3CH_2Cl in the presence of a small amount of oxygen over supported chromium based catalysts. We specially studied the effect on the activity, selectivity and stability of chromium oxide catalyst and modified by small amount of zinc supported over partially fluorinated alumina. The total amount of the active species on the support was fixed at 10 wt%. The aim was to promote the main fluorination reaction and to inhibit the secondary reactions. The Deacon reaction was studied over these catalytic systems.

Main reaction:

$$CF_3CH_2Cl + HF \rightleftharpoons CF_3CH_2F + HCl \text{ Fluorination} \quad (1)$$

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Secondary reactions:

$$CF_3CH_2Cl \rightleftharpoons CF_2 = CHCl + HF \text{ Dehydrofluorination} \quad (2)$$

$$O_2 + 4HCl\ 2Cl_2 + 2H_2O \text{ Deacon reaction} \quad (3)$$

2. Results and discussion

The transformation of CF_3CH_2Cl, in the presence of dioxygen was studied at 380 °C and atmospheric pressure and an HF/CF_3CH_2Cl ratio of 4.

The presence of small amount of oxygen (2%) in the feed prevents and stabilizes the deactivation of the chromium oxide supported over partially fluorinated alumina (noted AlF_3) (Fig. 1). Indeed, the presence of dioxygen slows down the catalyst deactivation of Cr/AlF_3. However, in this case, the activity for the fluorination reaction of CF_3CH_2Cl leading to the formation of CF_3CH_2F decreased strongly. This could correspond to a competitive adsorption of the various reactants on the same active sites (unsaturated coordinatively chromium species). Conversely, an increase of the activity for the formation of CF_3CH_2F was noticed when a small amount of zinc (Zn/Zn+Cr = 0.15) was added to the chromium based catalyst. As reported previously [16], the presence of zinc increases the number of the active sites and modified their strength. These sites were less sensitive to the presence of dioxygen. The Deacon reaction was observed by reaction between HCl produced by Cl/F exchanges and the dioxygen introduced in the feed (Fig. 2). Hydrochloric acid and oxygen were injected into stoichiometric (HCl/O_2 = 4) amount. The amount of HCl was 10 times greater than the amount of HCl produced from the conversion of 8% of CF_3CH_2Cl. These conditions were established to have a good gas chromatography analysis. First of all, we have verified that the same products were formed whatever the amount of HCl introduced. The Deacon reaction was higher over Cr/AlF_3 catalyst and decreased when the amount of zinc present in the catalyst increased. In the presence of CF_3CH_2Cl, the activity for the Deacon reaction decreased significantly whatever the catalyst composition. Under these conditions, the fluorination of CF_3CH_2Cl into CF_3CH_2F is the main reaction (Fig. 3). The catalyst containing a low amount of zinc (Zn/Zn+Cr = 0.15) remains the most active material for the formation of the fluorinated product. The decrease of the formation of CF_3CH_2F in the presence of dioxygen could be explained by the formation of new by-products involving the Deacon reaction as alkenes ($CHCl{=}CCl_2$, $CFCl{=}CHCl$ (Z and E)) and saturated halogenated hydrocarbons (CF_3CHCl_2, CF_3CHClF, CF_2ClCH_2Cl) (Fig. 4).

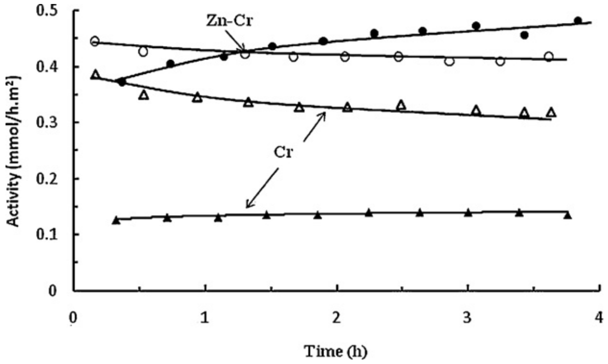


Fig. 1. Transformation of CF_3CH_2Cl alone or in the presence of dioxygen over Cr/AlF_3 (10 wt%) and $Zn\text{-}Cr/AlF_3$ (Zn/Zn+Cr = 0.15) catalysts (HCl/O_2 = 4/1, HF/CF_3CH_2Cl = 4, 380 °C). Full symbols: with dioxygen in the feed, Empty symbols: without dioxygen.

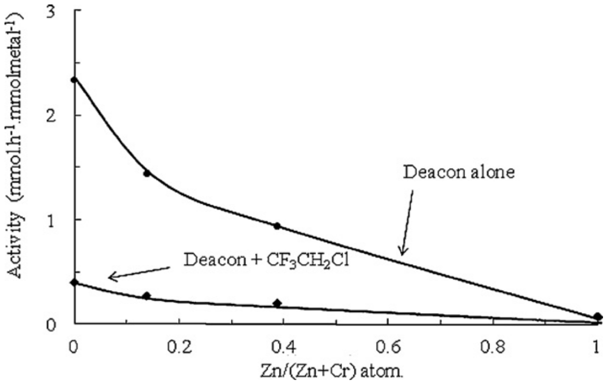
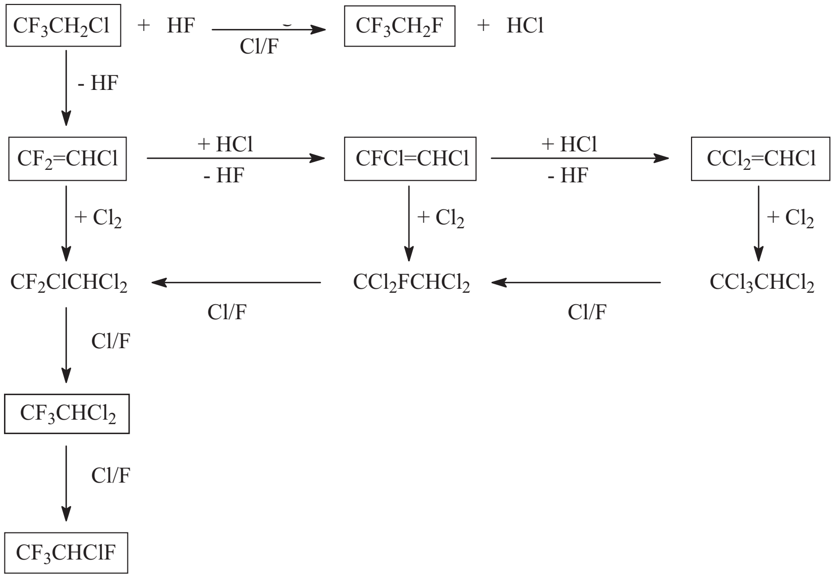


Fig. 2. Deacon reaction studied alone or simultaneously with the transformation of CF_3CH_2Cl. Effect of the Zn/(Zn+Cr) ratio (HCl/O_2 = 4/1, HF/CF_3CH_2Cl = 4, 380 °C).

According to previous works [18,19], the reaction scheme of the transformation of CF_3CH_2Cl could be completed with the new



Scheme 1. Transformation of CF_3CH_2Cl in the presence of a chromium based catalyst and dioxygen in the feed. Products detected and identified by GC–MS are boxed.

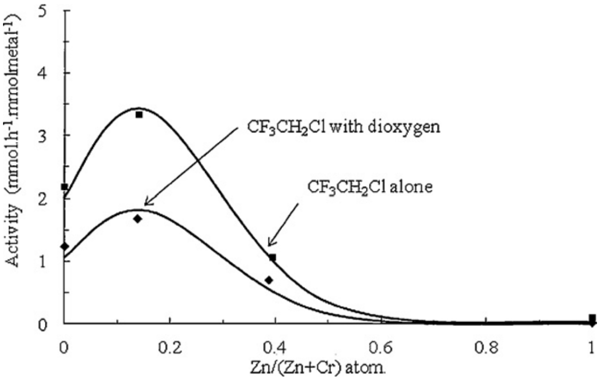


Fig. 3. Transformation of CF_3CH_2Cl alone or in the presence of dioxygen. Formation of CF_3CH_2F. Effect of the Zn/(Zn+Cr) ratio (HCl/O_2 = 4/1, HF/CF_3CH_2Cl = 4, 380 °C).

products observed in the presence of dioxygen (Scheme 1). Different reactions are involved:

- The fluorination reaction of CF_3CH_2Cl into CF_3CH_2F involving Cl/F exchange,
- The dehydrofluorination reaction (or elimination of HF) leading to the formation of $CF_2{=}CHCl$, main by-product of CF_3CH_2Cl. The formation of secondary olefins such as $CFCl{=}CHCl$ (E and Z) and $CCl_2{=}CHCl$, was then obtained by addition of HCl followed by removal of HF, these alkenes were produced in very low amount.
- The Deacon reaction leading to the formation of Cl_2 by reaction between dioxygen and hydrogen chloride formed during the Cl/F exchange of CF_3CH_2Cl into CF_3CH_2F. The addition of dichlorine into $CF_2{=}CHCl$ led to the formation of $CF_2ClCHCl_2$ which could be fluorinated into CF_3CHCl_2 by Cl/F exchange. All of these products were identified by GC–MS.

The selectivity towards the fluorination reaction (F) (corresponding to the formation of CF_3CH_2F) was calculated by the ratio between the fluorination reaction and the various reactions (Fluorination reaction (F), Deacon reaction (D), formation of alkenes (A) and Chlorinated products (C)). This selectivity towards the formation of CF_3CH_2F is favored in the presence of a small addition of zinc (atomic ratio Zn/(Zn+Cr) = 0.15) (Fig. 5). These results confirmed the promoting effect of zinc in the presence of dioxygen which represents conditions close to process conditions.

However, the formation of alkenes decreases as the amount of zinc increases (Fig. 3). The role of zinc could be related to various phenomena according to the literature. Indeed, the presence of zinc would decrease the strength of Lewis acidity of unsaturated coordinatively chromium atoms and favors the adsorption of the substrate (CF_3CH_2Cl) by the chlorine atom for the Cl/F exchange. The fluorination reaction is then favored over the reaction dehydrofluorination. Indeed, measurements of pyridine adsorption followed by infra-red spectroscopy showed that the addition of zinc reduced the acid strength of chromium atoms. In addition, Bonniface et al. [15] showed by isotopic exchange with fluorine ^{19}F that the presence of zinc alter the adsorption of HF (nucleophilic source) to the solid surface, making it more labile. In agreement with our results, this would result in a decrease in the apparent activation energy in the presence of small addition of zinc [21]. Moreover, the fluorination and Deacon reactions involve the same actives sites and these two reactions were in competition and promoted with the presence of zinc (Zn/Zn+Cr = 0.15). However, the fluorination is more promoted and the selectivity towards fluorination is higher. Indeed, a competitive adsorption between CF_3CH_2Cl and O_2 and HCl could explain these results, the adsorption of CF_3CH_2Cl being stronger.

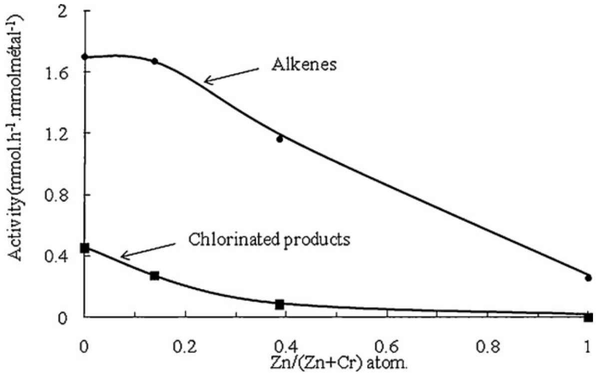


Fig. 4. Transformation of CF_3CH_2Cl Formation of by-products (alkenes and chlorinated products). Effect of the Zn/(Zn+Cr) ratio (HCl/O_2 = 4/1, HF/CF_3CH_2Cl = 4, 380 °C) (HCl/O_2 = 4/1, HF/CF_3CH_2Cl = 4, 380 °C).

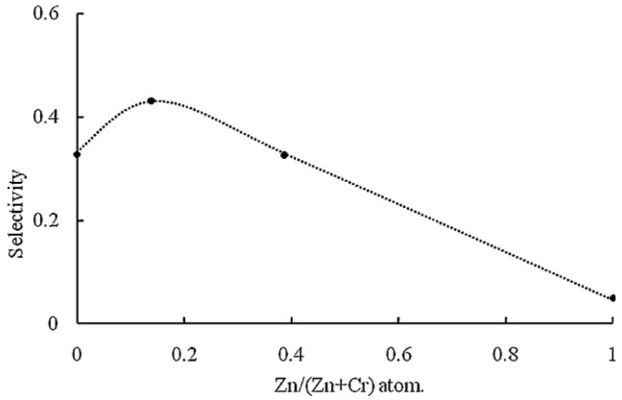


Fig. 5. Transformation of CF_3CH_2Cl in the presence of dioxygen. Effect of the Zn/(Zn+Cr) ratio on the selectivity ((F/(F+D+A+C), F: Fluoration, D: Deacon, A: Alkenes et C: chlorinated by-products).

3. Conclusion

Based on our finding, the presence of dioxygen has a positive effect on the catalyst stability of the pure chromium catalyst However, the selectivity towards CF_3CH_2F decreased due to the presence of the Deacon reaction. The activity of the catalyst containing a low amount of zinc increased and confirm the positive effect of zinc to chromium based catalyst measured only for the transformation of CF_3CH_2Cl alone by decreasing the Lewis acidity of the active sites.

4. Experimental

4.1. Catalysts and chemicals

The commercial alumina was fluorinated by HF at 400 °C in order to obtain a partial fluorinated support which was stabilized under fluorination conditions [18] with a surface area of around 45 m^2/g.

Zinc-doped chromium oxide catalysts supported over partially fluorinated alumina (55% of AlF_3) were prepared by wetness impregnation of the fluorinated alumina with an aqueous solution of chromic anhydride, zinc chloride and methanol [16]. The reduction of Cr^{VI} into Cr^{III} was carried out in the presence of methanol. The impregnation of AlF_3 was carried out at room temperature and atmospheric pressure. The quantities of chromium and zinc corresponded to a total amount of added components

(Zn+Cr) of around 10 wt% and atomic ratios of Zn/(Zn+Cr) equal to 0, 0.15, 0.33, 1. Then the various catalysts were dried at 110 °C during one night under atmospheric pressure. The precursors were decomposed during the fluorination of the catalyst by HF at 380 °C during 2 h in a dynamic flow reactor to produce the corresponding fluorinated or oxyfluorinated materials. Chemical analyses of the elements (chromium, zinc) were carried out after the fluorination step.

No significant variation of the specific surface could be noticed whatever the catalyst after the treatment by HF during 2 h, as reported in a previous paper [16].

Anhydrous Chromic anhydride (99%) was purchased from Merck, zinc chloride (98%) from Riedel-deHaën and methanol (99.8%) from SDS. They were used without further purification.

4.2. Catalytic measurements and analysis

The transformation of CF_3CH_2Cl was carried out under atmospheric pressure in a fixed bed reactor at 380 °C. All the reactants were diluted in helium. The flow rate of CF_3CH_2Cl was regulated at 50 °C (to avoid any condensation) by a Brooks mass flowmeter. The helium, O_2 and HCl feeds were regulated at room temperature by a Brooks mass flowmeter. The catalyst (sieved to a diameter between 0.250 mm and 0.315 mm) was mixed with 6 cm^3 of Lonza graphite. When the reaction products emerged from the reactor they were washed successively in two flasks containing water and then in one containing potassium hydroxide (1 M) to neutralize the unreacted hydrogen fluoride and HCl produced by Cl/F exchanges. They were then dried on a 4 Å molecular sieve. The organic reaction products were analyzed on line with a gas chromatograph (Varian GC 3400) equipped with a flame ionization detector and a DB5 capillary column (J and W Scientific). O_2, HCl and Cl_2 were analyzed on line with a gas chromatograph equipped with a catharometer detector and a DB5 capillary column (J and W Scientific). HCl and dioxygen were injected into stoichiometric ($HCl/O_2 = 4$) ratio.

The various activity was calculated as defined: A (mmol/h/g) = F^*y/weight of catalyst with F: flow of the reactant (mmol/h), y: yield of each product (mol%).

The activity in mmol/h/mmol metal was obtained by divided the activity by the total amount of metal.

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