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Effect of acid strength of co-precipitated chromia/alumina catalyst on the conversion and selectivity in the fluorination of 2-chloro-1,1,1-trifluoroethane to 1,1,1,2-tetrafluoroethane[1]

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Abstract

Different fluorinated catalysts based on co-precipitated Cr_2O_3/Al_2O_3 and doped with compounds of Zn and/or Mg are prepared and their total acidity determined by TPD of ammonia. The influence of acidity of the above catalysts on the conversion and selectivity in the fluorination of HCFC-133a to give HFC-134a was studied. It was found that the selectivity for HFC-134a increases with a fall in the relative percentage of strong acid centres. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The fluorination of 2-chloro-1,1,1-trifluoroethane (HCFC-133a) with anhydrous hydrogen fluoride (AHF) in the presence of a suitable halogen exchange catalyst [1] is of commercial interest to produce 1,1,1,2-tetrafluoroethane (HFC-134a), a compound recommended to replace some of the ozone depleting chlorofluorocarbons [2]. Several precatalyst formulations based on bulk Cr_2O_3 or mixed oxide Cr_2O_3/Al_2O_3 with and without promoters were developed. The precatalysts were first fluorinated with AHF to generate in situ the active catalyst.

The selectivity for HFC-134a in the fluorination of HCFC-133a with AHF is affected because of side reactions leading to the formation of 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), pentafluoroethane (HFC-125), 1,1,1-trifluoroethane (HFC-143a), 2-chloro-1,1-difluoroethene (HCFC-1122) and trichloroethylene (TRI). The formation of pentahalo compound [3] (HCFC-124) was attributed to the chlorination of HCFC-133a by elemental chlorine generated through the occurrence of Deacon reaction between HCl and Cr_2O_3. An alternate mechanism proposes dismutation reaction [4] of HCFC-133a to give HFC-143a and HCFC-123. The latter is a precursor to HCFC-124 and HFC-125. The dehydrohalogenation of HCFC-133a to give HCFC-1122 is a competitive reaction [5] dependent on temperature. The factors relating the catalytic activity in terms of conversion of HCFC-133a were investigated for catalysts based on Cr_2O_3. Webb and Winfield [6,7] postulated the formation of a labile chromium oxyfluoride as responsible for halogen exchange. TPR and TPO studies [5,8–10] on bulk Cr_2O_3 showed that the catalytic activity depends on the number of reversibly oxidizable sites. Kemnitz et.al [11,12] attribute the activity to the formation of β-CrF_3. In the case of catalysts based on Al_2O_3, the formation of β-AlF_3 was considered important [13].

Based on TPD studies [9,14] it was proposed that Lewis acid sites are responsible for catalytic activity. All the above studies relate to the conversion of HCFC-133a. In this paper we report our study on the effect of the acid strength of co-precipitated Cr_2O_3/Al_2O_3 with and without doping with compounds of Zn and/or Mg on the conversion and selectivity in the fluorination of HCFC-133a to give HFC-134a. A co-precipitated Cr_2O_3/Al_2O_3 was chosen as base catalyst because it meets the strength requirement for operation under pressure as compared to bulk Cr_2O_3. Compounds of Zn and Mg are chosen as dopants because of their known promotional effects.

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2. Experimental

The surface area was determined by the BET method from the adsorption isotherms of nitrogen at liquid nitrogen temperature with the help of Sartorius Gravimat. The X-ray data were collected using a Siemens D5000 X-ray powder diffractometer with Cu K_α radiation.

2.1. Preparation of catalyst

2.1.1. Co-precipitated Cr_2O_3/Al_2O_3 (catalyst A)

$Cr(NO_3)_3 \cdot 9H_2O$ (130.8 g) and $Al(NO_3)_3 \cdot 9H_2O$ (458.8 g) were dissolved in 6 l of distilled water and the hydroxides were precipitated using 1 M NH_4OH as described in literature [15]. The gel obtained was filtered, washed free from nitrate ion, dried overnight in an oven at 120°C, shaped into 3 mm extrudates and calcined at 400°C in nitrogen atmosphere for 6 h. Chemical composition and surface area are given in Table 1. X-ray diffraction analysis indicates the amorphous nature of the catalyst except for traces of γ-Al_2O_3.

2.1.2. $ZnCl_2/Cr_2O_3/Al_2O_3$ (catalyst B)

Extrudates of catalyst A (60 g) were suspended in a solution of $ZnCl_2$ (5 g) in 54 ml distilled water. The mixture was slowly vaporized in vacuum in a rotavapor to dryness. The solid obtained was dried at 120°C for 12 h and calcined at 400°C in nitrogen atmosphere for 16 h. The chemical composition and surface area are given in Table 1. X-ray diffraction analysis showed the amorphous nature of the catalyst except for traces of γ-Al_2O_3.

2.1.3. $MgCl_2/Cr_2O_3/Al_2O_3$ (catalyst C)

Extrudates of catalyst A (141 g) were suspended in a solution of $MgCl_2 \cdot 6H_2O$ (6 g) in 110 ml distilled water and then processed as described in Section 2.1.2 above. The chemical composition and surface area are given in Table 1.

2.1.4. $MgO/ZnO/Cr_2O_3/Al_2O_3$ (catalyst D)

Aq.solutions (10%) were made separately by taking $Mg(NO_3)_2 \cdot 6H_2O$ (6.33 g) $Zn(NO_3)_2 \cdot 6H_2O$ (1.82 g), $Cr(NO_3)_3$, $9H_2O$ (23.1 g) and $Al(NO_3)_3 \cdot 9H_2O$ (83.44 g) in distilled water and then mixed together. Then 7 M NH_4OH solution was added drop wise with vigorous stirring, till pH of the solution attain 9 during precipitation. The co-precipitated metal hydroxides were filtered, washed free from nitrate ion, dried at 170°C for 12 h in an oven, shaped into tablets and calcined at 380°C in nitrogen atmosphere. X-ray diffraction analysis revealed the amorphous nature of the catalyst except for traces of γ-Al_2O_3. surface area 170 m^2/g.

2.1.5. Fluorination

The apparatus consists of a fixed bed reactor system which could be operated both at atmospheric and also at high pressures. Anhydrous hydrogen fluoride and HCFC-133a were drawn in vapor form from pressure cans. The feed rates were monitored continuously by mounting the containers on separate balances. The flows of AHF and HCFC-133a were regulated by means of needle valves.

The precatalyst (20 g) after charging into the reactor was first treated with nitrogen and then fluorinated with AHF at atmospheric pressure. The fluorination of HCFC-133a was carried out under a pressure of 90 psi±5. The product stream was scrubbed with aqueous KOH, then passed through a drier and condensed in a dry ice acetone cooled receiver. During the initial period of reaction, the recovery of the product is not quantitative due to solubility in aqueous alkali. However, after saturation steady state is reached and no loss in material balance was observed within the limits of experimental error. The composition of the product stream was estimated by GC(HP) Model 5890 series II using a 12 ft×1/8 in. SS column packed with porapak Q, (carrier gas, He, 30 ml/min. Column temperature: 100–10°C/min - 230°C and FID detector). The relative composition of the products is based on peak areas and therefore do not represent the absolute yields because of difference in response factors.

3. Results and discussion

The reaction of interest in the fluorination of 2-chloro-1,1,1-trifluoroethane(HCFC-133a) is the halogen exchange to give 1,1,1,2-tetrafluoroethane (HFC-134a). It is known that this reaction is accompanied by other processes depending upon the catalyst and reaction conditions. The reaction leading to HFC-134a and the side products that contribute to the lowering of selectivity are depicted in Scheme 1.

It has been reported that the conversion of HCFC-133a to HFC-134a is thermodynamically restricted to not more than 30% [5,8]. The fluorination of HCFC-133a using catalyst A gave 34% conversion but the selectivity for HFC-134a was only 77% (see Table 2). The low selectivity is due to the

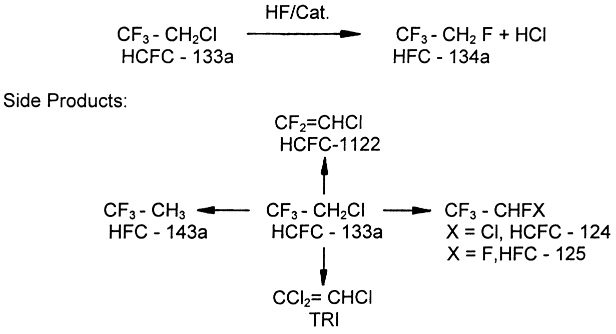
Table 1
Composition and surface area of catalyst

Precatalyst	Mg (%)	Zn (%)	Cr (%)	Al (%)	Surface area (m^2/g)
Cr_2O_3/Al_2O_3 (catalyst A)	–	–	17.80	39.17	228
$Zn/Cr_2O_3/Al_2O_3$ (catalyst B)	–	3.40	15.60	37.11	170
$MgCl_2/Cr_2O_3/Al_2O_3$ (catalyst C)	0.50	–	17.45	38.40	198
$MgO/ZnO/Cr_2O_3/Al_2O_3$ (catalyst D)	3.33	2.22	16.67	33.33	170

Table 2
Effect of acid strength of the catalyst on the fluorination of HCFC-133a to HFC-134a at 350°C

Precatalyst	Total acidity	Relative acidity (%)		Conversion of HCFC-133a (%)	Selectivity for HFC-134a (%)
		200–400°C	400–500°C		
Cr_2O_3/Al_2O_3 (catalyst A)	597	53	47	34	77
$ZnCl_2/Cr_2O_3/Al_2O_3$ (catalyst B)	582	64	36	22	88
$MgCl_2/Cr_2O_3/Al_2O_3$ (catalyst C)	243	59	41	25	78
$MgO/ZnO/Cr_2O_3/Al_2O_3$ (catalyst D)	290	78	22	11	94

Mole ratio HF/HCFC-133a=6, Pressure=90 psi±5, *W/F*=70 g h/g mol.



Scheme 1.

formation of HFC-125. Assuming that the presence of strong acid centres are responsible for the side reaction giving rise to HFC-125, a study has been made to evaluate the activity of different catalysts with different acid strengths.

A set of precatalysts consisting of co-precipitated Cr_2O_3/Al_2O_3 doped with compounds of Zn and/or Mg were prepared (catalysts B–D) and their total acidity was determined by TPD of ammonia. Zinc [13,16,17] and magnesium [18,19,20] compounds were chosen as dopants because of the reports that they both promote the catalyst activity. The acidity of these catalysts prepared in the manner described here decreased after doping with Zinc or Magnesium as compared to the base catalyst. These were fluorinated and then used for the reaction of HCFC-133a to give HFC-134a. The results are given in the table.

The results show that a fall in total acidity of the precatalyst used exhibits a fall in conversion but no quantitative relationship is found. Between the catalysts C and D the former exhibits higher conversion inspite of lower acidity. The results indicate that a reduction in the strong acid centres relative to the total acidity is one of the factors that gives rise to an increase in selectivity, by the suppression of dismutation reaction.

4. Conclusions

The fluorination of HCFC-133a to HFC-134a both containing four halogens, on co-precipitated Cr_2O_3/Al_2O_3 is accompanied by the formation of HFC-143a and HFC-125 which contain three and five halogens, respectively. Their formation appears to depend on the strong acid sites. The formation of pentahaloethanes can be suppressed by doping the co-precipitated Cr_2O_3/Al_2O_3 with compounds of Zn or Mg, thus increasing selectivity to HFC-134a. There is a fall in conversion after doping with Zn or Mg. One of the factors responsible for this appears to be the fall in total acidity. The increase in selectivity is attributed to the relative lowering of the percentage of strong acid centres.

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