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A Comparative Study of Bulk and Supported Chromia Catalysts for the Fluorination of Trichloroethylene

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The photoelectron spectroscopy of Cr_2O_3 and impregnated Cr_2O_3/Al_2O_3 catalysts was studied before and after treatment with anhydrous hydrogen fluoride (AHF) and after reaction of trichloroethene (TRI) with AHF. XPS results indicate formation of both hydroxyfluorides and fluorides of Cr and Al. The binding energy values of the $Cr2p_{3/2}$ levels of oxides, and also of fluorinated species, were found to be different in bulk and supported catalysts. The fluorinated catalysts from Cr_2O_3 and impregnated and coprecipitated Cr_2O_3/Al_2O_3 exhibit the same order of activity in the fluorination of TRI in terms of conversion and selectivity to 2-chloro-1,1,1-trifluoroethane but they differ in life span. Bulk Cr_2O_3 exhibits a longer life span.

Key Words: **fluorination; chromium oxide; ESCA; hydrochlorofluoroalkanes.**

INTRODUCTION

The catalytic vapor-phase fluorination of volatile chloroorganics with anhydrous hydrogen fluoride (AHF) has gained importance in the synthesis of ozone-benign hydrofluorocarbons (HFCs) to replace chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). 1,1,1,2-Tetrafluoroethane (HFC-134a) is one of the important CFC substitutes and is prepared from trichloroethene (TRI) via the intermediate 2-chloro-1,1,1-trifluoroethane (HCFC-133a).

Most of the work leading to the discovery and development of a suitable and efficient catalyst for fluorination is covered in the patent literature (1). In the begining metals such as Cr, Co, Ni, Fe, and Pd impregnated on Al_2O_3 were fluorinated and used as catalysts for the halogen exchange reaction (2). Although Al_2O_3 itself acts as a catalyst, the activity was enhanced by impregnation with salts (3) of Cr, Co, Ni, Cu, and Pd. An early breakthrough was obtained for the first time in the fluorination of TRI using CrF_3 (4). The formation of HFC-134a in trace amounts was reported for the first time in the fluorination of TRI. The interest in Cr-based catalysts led to the discovery of fluorinated Cr_2O_3 as a metathetical exchanger of chemically bound halogens (5). However, the active species generated by fluorination of Cr_2O_3, which is responsible for catalytic activity, has yet to be characterized fully. In analogy to the reaction of HCl with Cr_2O_3 (Deacon reaction) (6), where CrOCl is formed, it was postulated that an oxyfluoride of chromium could be formed by reaction with HF. Estimation of the elemental composition of fluorinated Cr_2O_3 gave the empirical formula (7) CrO_xF_y (x and y can have values in the range 1–2).

The mechanistic studies (8) on vapor-phase catalytic fluorination of chloroorganics have two concerns, the reaction pathway and the nature of the active sites on the catalyst. In the specific case of the synthesis of HFC-134a from TRI, the first step involves Markownikov's addition of HF to give 1-fluoro-1,1,2-trichloroethane (HCFC-131a). Thereafter, the replacement of Cl by F occurs preferentially at the CCl_2F group via two independent pathways. One of them involves a metathetical halogen exchange and the other an elimination–addition reaction (9–11). The complete sequence is depicted in Scheme 1. All reactions have been shown to proceed reversibly (12), the direction depending on the concentration of the hydrogen halide. Catalyst characterization studies carried out by different groups led to the following conclusions. Webb and Winfield (13, 14) used labeled HF to fluorinate Cr_2O_3 and postulated the formation of three different species, among which a reversibly oxidizable oxyfluoride is responsible for halogen exchange. Blanchard and co-workers (15, 16) studied the TPR and TPO of the precatalyst Cr_2O_3 and showed that the catalytic activity depends on the reversibly oxidizable sites, the efficiency increasing with the increasing number of such centers. The investigations led by Kemnitz *et al.* (17, 18) showed that the catalytic activity depends on the formation of β-CrF_3. The TPD studies (19, 20) revealed the dependence of the catalyst activity on the Lewis acid sites. Having recourse to the different studies outlined above, we have undertaken a study on the nature and performance of

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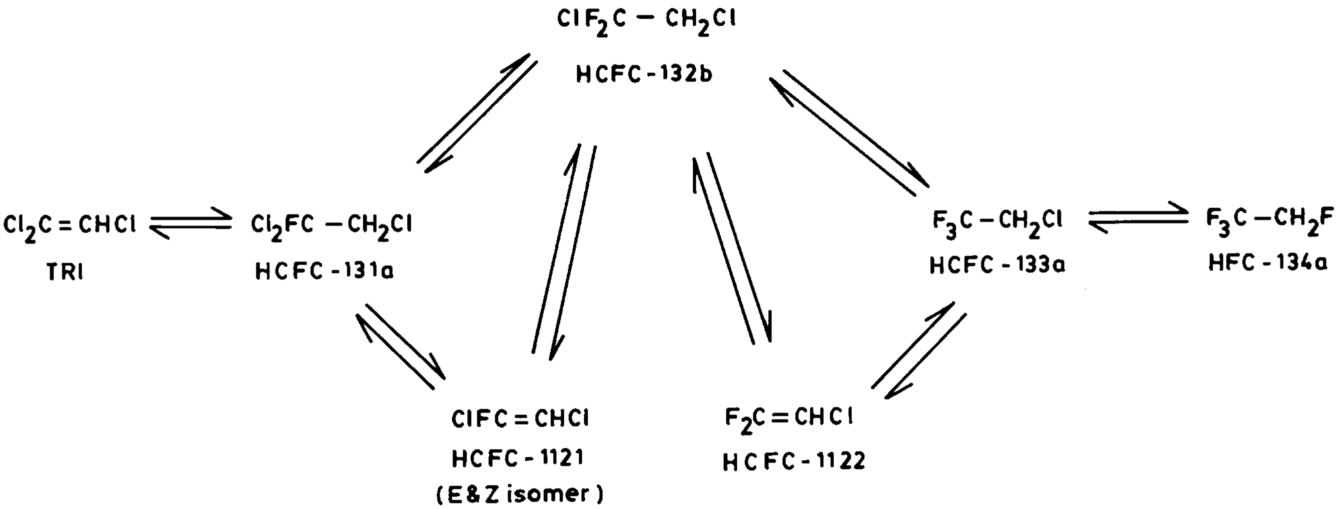

SCHEME 1. Reaction pathway for formation of HFC-134a by fluorination of TRI.

chromia alone and chromia-alumina-based catalysts in the fluorination of TRI to HCFC-133a.

EXPERIMENTAL

1. Preparation of Catalysts

1.1. Chromia, Cr_2O_3 (catalyst A). The procedure described in the literature (21) was followed to obtain CrOOH gel, which was dried, shaped into 4-mm-diameter tablets, and then calcined at 400°C for 24 h in nitrogen atmosphere. The catalyst obtained was X-ray amorphous, SA 152 m^2/g.

1.2. Impregnated Cr_2O_3/Al_2O_3 (catalyst B). Extrudates of γ-Al_2O_3 (UCIL, SA 200 m^2/g) were subjected to multistep impregnation with a solution of chromic acid, dried overnight in an oven at 120°C, and calcined at 450°C for 24 h in nitrogen. The calcined catalyst was analyzed and found to contain 18.2% Cr, of which Cr^{6+} was 2.17%, SA 147 m^2/g.

1.3. Coprecipitated Cr_2O_3/Al_2O_3 (catalyst C). $Cr(NO_3)_3 \cdot 9H_2O$ (130.8 g), and $Al(NO_3)_3 \cdot 9H_2O$ (458.8 g), were dissolved in 6 L distilled water and the hydroxides were precipitated using 1 M NH_4OH as described in literature (22). 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 analysis revealed 17.8% Cr content in the conditioned Cr_2O_3/Al_2O_3 catalyst. X-ray diffraction analysis indicated the amorphous nature of the catalyst except for traces of γ-Al_2O_3, SA 228 m^2/g.

2. Fluorination

The apparatus consisted of a fixed bed reactor system. TRI was fed into the reactor via a vaporizer using a diaphragm-operated metering pump. Anhydrous hydrogen fluoride was drawn in vapor form from pressurized cans. All feed rates were monitored continuously by mounting the containers on separate balances. The flow of AHF was regulated by means of needle valves.

The precatalyst (20 g), after being charged into the reactor, was first treated with nitrogen and then fluorinated with AHF initially at 150°C for 4 h and finally at 375°C for 72 h. The catalyst bed temperature was brought to 300°C and the fluorination of TRI carried out. The product stream was scrubbed with aqueous KOH, passed through a drier, and condensed in a dry ice–acetone cooled receiver. During the initial period of reaction, the recovery of the product was not quantitative due to solubility in aqueous alkali. However, after saturation, the steady state was reached and no loss in material balance was observed within the limits of experimental error. The composition of the product stream was estimated by drawing online samples periodically and analyzing them by gas chromatography (HP Model 5890 Series II) using a 12 ft × 1/8-in. S S column packed with Porapak Q (carrier gas, He at 30 ml/min; column temperature, 100–230°C at 10°C/min; and FID detector). The relative composition of the products is based on peak areas.

3. X-Ray Photoelectron Spectroscopic Studies (ESCA)

XPS measurements were made with a V G Scientific (UK) ESCA-3 MK-2 electron spectrometer using a nonmonochromatic Mg$K\alpha$ radiation (1253.6 eV). The binding energy (BE) scale was calibrated by determining the BE of the Au$4f_{7/2}$ (84 eV) level. All the spectra were recorded under the same spectrometer parameters of 4 mm entry split and 50 eV pass energy. The instrument was operated under vaccum better than 10^{-9} Torr. The position of C1*s* BE at 285 eV was used as an internal standard for correcting any charge-induced peak shifts.

For all the samples Cr2*p*, Al2*s*, O1*s*, and F1*s* levels were recorded. A wide scan of all the samples did not show any lines other than the expected ones, indicating the absence of

TABLE 1

Binding Energy Values and the Atomic Ratios of the Reference Compounds

	Binding energy (eV)			Atomic ratio		
Compound	Cr2$p_{3/2}$	O1*s*	F1*s*	Cr/O	F/Cr	O II/F
Cr_2O_3	576.3	530.0 531.9	—	0.6	—	—
CrO_3	576.2 579.3	530.5 533.0	—	0.3	—	—
$CrF_3,4H_2O$	579.6	531.7 533.4	684.8	—	3.2	1.1
$CrF_3,4H_2O^a$	578.9 580.3	531.0 533.2	684.5	—	1.8	0.6

[a] After being heated in air.

surface impurities. Most of the peaks either were very broad or exhibited asymmetry, indicating multiple peak structure. In such cases peak synthesis was performed using a nonlinear least-squares method to fit the data. The curves were resolved using a Gaussian function and an appropriate combination of peak height, linewidth (FWHM—full width at half maximum), and peak position. Peak intensities were calculated by integrating the peak area after proper background subtraction of the baseline. The error in the measurement of BE values would be nearly ±0.2 eV.

RESULTS AND DISCUSSION

The photoelectron spectra of CrO_3 (used in the preparation of catalyst A), Cr_2O_3 and $CrF_3 \cdot 4H_2O$ (Aldrich Chemical Co.) were recorded to obtain the experimental BE values (Table 1) for reference purposes. Although the BE values are in good agreement with those reported in the literature (23), the atomic ratios do not exactly correspond to the theoretical values due to the presence of minor amounts of other chromium species in the sample.

TABLE 2

Binding Energy Values and Atomic Ratios of Catalyst A

	Binding energy (eV)			Atomic ratio	
Sample	Cr2$p_{3/2}$	O1*s*	F1*s*	Cr I + Cr II/O I	F/Cr II
Cr_2O_3 (Cat. A)	576.3 579.8	530.1 532.2	—	0.56	—
Fluorinated Cr_2O_3	576.3 578.4	531.0 533.2	684.6	0.71	2.1
After 26 h fluorination reaction of TRI	576.7 579.5	530.6 533.1	684.8	0.83	3.8

Catalyst A

Table 2 summarizes the results of ESCA studies on catalyst A. The Cr2$p_{3/2}$ peak (Fig. 1A) shows a clear asymmetry and was resolved into two peaks with maxima at 576.3 and 579.8 eV. The peaks were assigned to Cr^{3+} and Cr^{6+}, referred to as Cr I and Cr II, respectively. The surface seems to be saturated with higher oxides and the relative percentages of Cr^{3+} and Cr^{6+} were estimated to be 62 and 38%. The Cr I + Cr II/O I molar ratio was 0.56. The O1*s* core level was resolved into two peaks with BE values 530.1 and 532.2 eV (Fig. 1B). Since oxygen in both Cr_2O_3 and CrO_3 is in the −2 oxidation state, the BE of the O1*s* level in both is expected to be nearly the same. The peak at 530.1 eV was assigned to oxygen present in Cr_2O_3 and CrO_3. Since the sample was exposed to air, we attribute the second oxygen peak to the presence of moisture on the surface.

Catalyst A was first treated with nitrogen for 3 h at 340°C, followed by fluorination with AHF at 350°C for 8 h, and flushed with nitrogen at 350°C until the exit gases did not

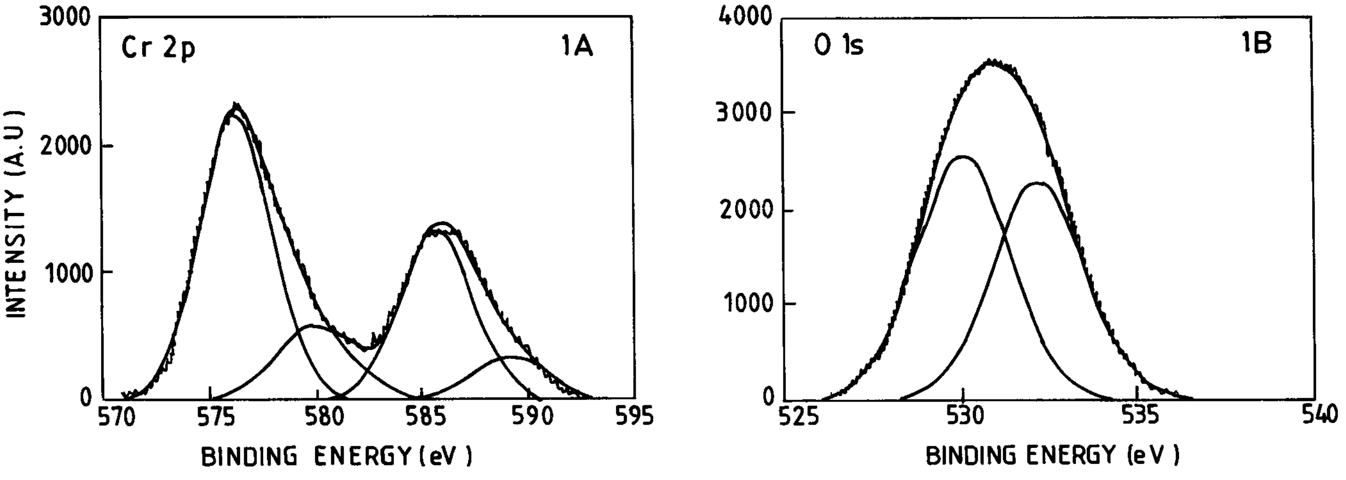

FIG. 1. ESCA spectrum of bulk Cr_2O_3: (A) BE of Cr2*p* levels, (B) BE of O1*s* levels.

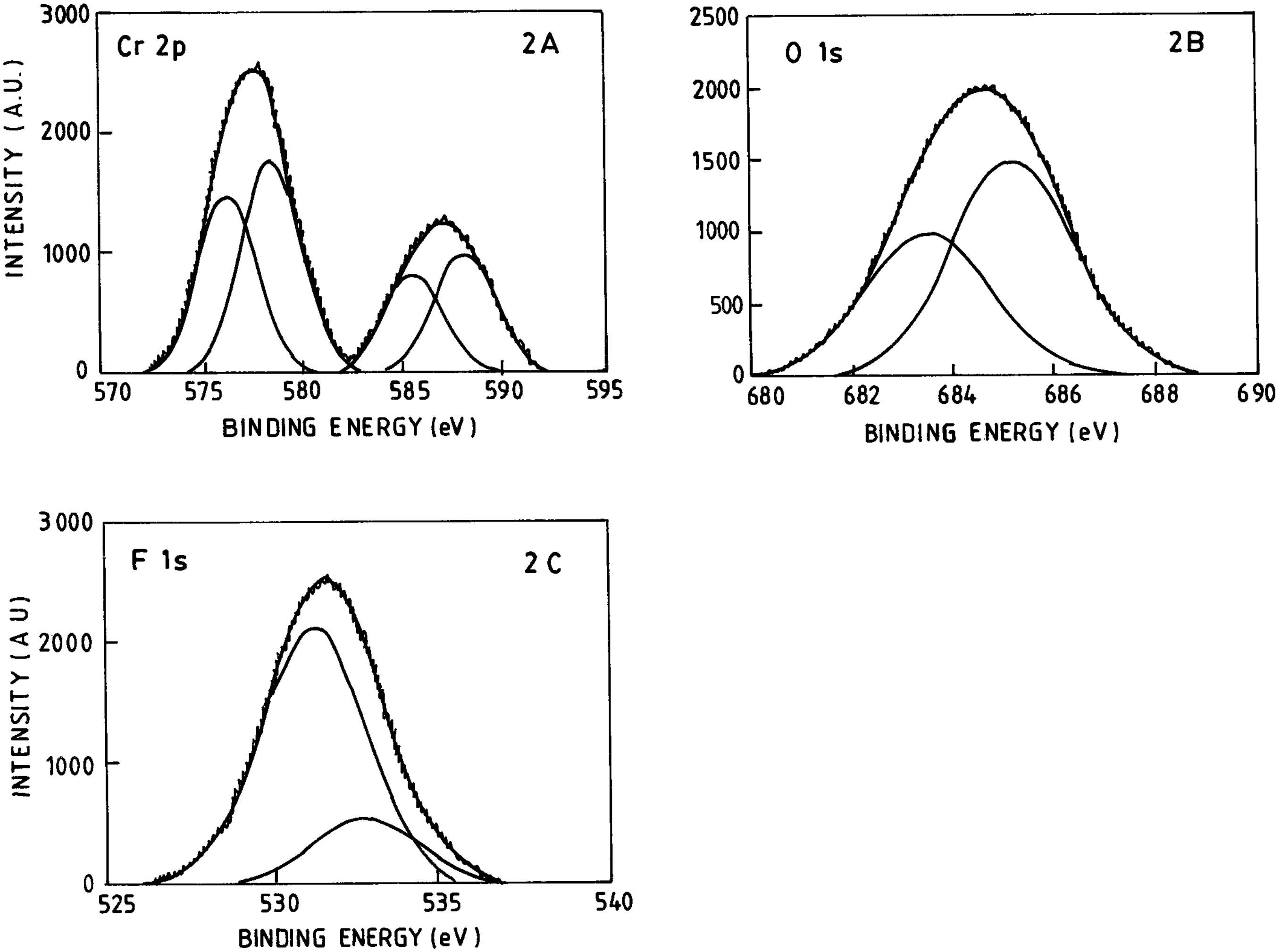

FIG. 2. ESCA spectrum of fluorinated Cr_2O_3: (A) BE of Cr2*p* levels; (B) BE of O1*s* levels; (C) BE of F1*s* levels.

show the presence of HF. The spectra obtained for the $Cr2p_{3/2}$, O1*s*, and F1*s* levels are depicted in Figs. 2A, 2B, and 2C, respectively, and the data are summarized in Table 2. The $Cr2p_{3/2}$ level (Fig. 2A) was resolved into two peaks, with maxima at 576.3 (Cr I) and 578.4 (Cr II) eV assignable to the presence of unreacted Cr_2O_3 and chromium bonded to F, respectively. The F1*s* level was observed at 684.6 eV. The ratio F/Cr II was found to be 2, which suggests that the compound formed could be $Cr(OH)F_2$. The probable pathway for the formation of $Cr(OH)F_2$ is given in the equations below:

$$Cr_2O_3 + 2HF \rightarrow 2CrOF + H_2O$$

$$CrOF + HF \rightarrow Cr(OH)F_2$$

$$Cr(OH)F_2 + HF \rightarrow CrF_3 + H_2O.$$

The O1*s* spectrum was resolved into two peaks with BE values 531.0 (O I) and 533.2 (O II) eV. The second oxygen peak at 533.2 eV was attributed to absorbed water generated during the fluorination. The BE values found here for Cr, O, and F differ from those reported by Brunet *et al.* (24) for fluorinated Cr_2O_3 prepared from $Cr(NO_3)_3$.

The active halogen-exchange catalyst (chromium oxyfluoride) can be generated by either oxygenation (4) of CrF_3 or fluorination (5) of Cr_2O_3 with HF. Considering this aspect, the commercially available $CrF_3 \cdot 4H_2O$ was heated in air at 400°C for a few hours and its XPS was recorded (see Table 1). During this process $CrF_3 \cdot 4H_2O$ not only loses water of hydration but also becomes oxygenated. The BE value for the $Cr2p_{3/2}$ level in $CrF_3 \cdot 4H_2O$ is 579.6 eV. After being heated in air, the sample gave two peaks at 578.9 and 580.3 eV. The peak at 578.9 eV is close to the $Cr2p_{3/2}$ level at 578.4 eV attributed to the formation of $Cr(OH)F_2$ after fluorination of Cr_2O_3. The peak at 580.3 eV may be due to the formation of chromium oxyfluoride, in which the metal is present in a higher oxidation state. X-rays of the sample obtained from $CrF_3 \cdot 4H_2O$ after heating in air did not show characteristic lines corresponding to CrF_3.

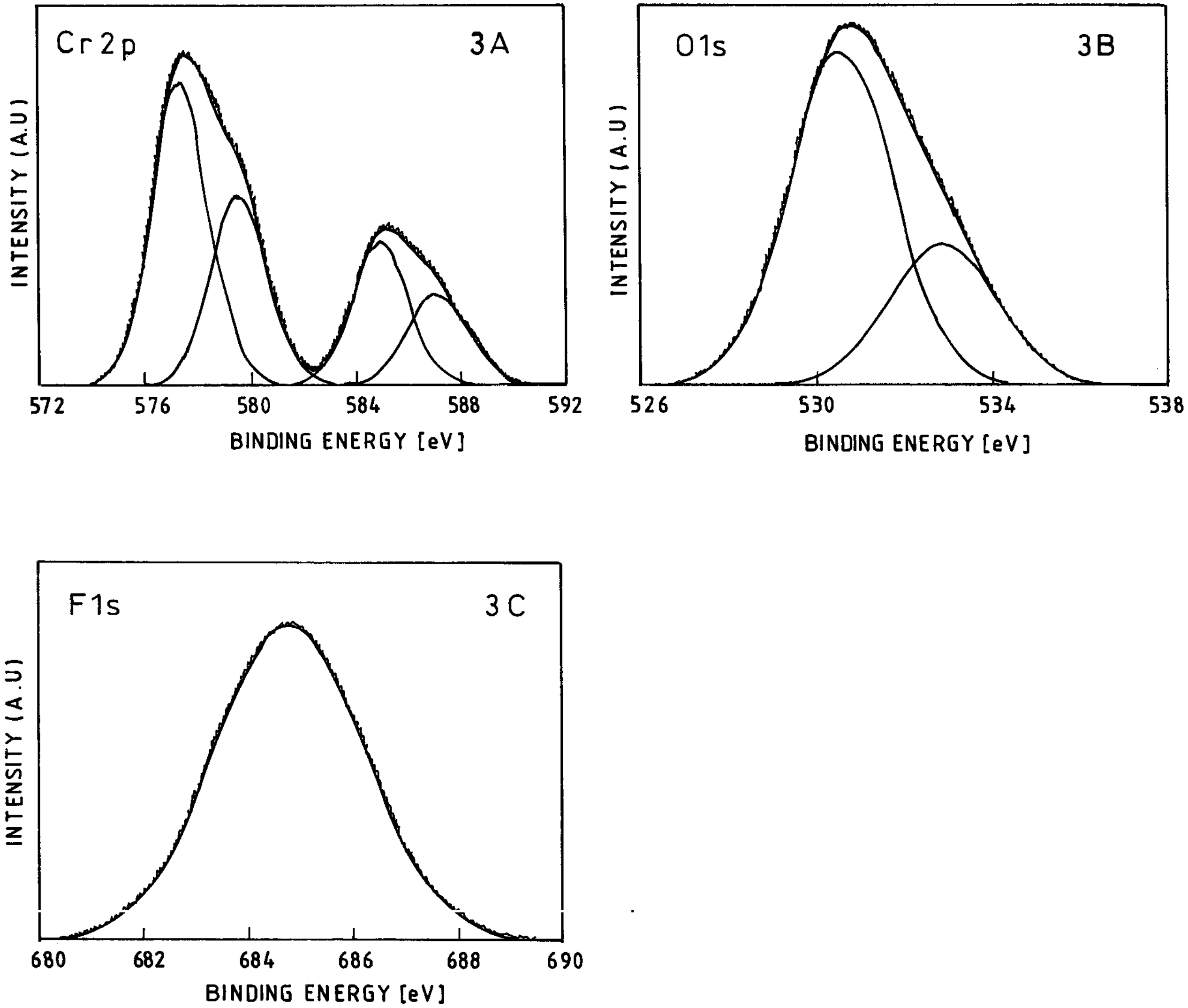

FIG. 3. ESCA spectrum of fluorinated Cr_2O_3 after 26 h reaction of TRI with AHF: (A) BE of Cr2*p* levels; (B) BE of O1*s* levels; (C) BE of F1*s* levels.

The fluorinated catalyst was further subjected to catalytic reaction of TRI with AHF for 26 h and then analyzed by XPS. The $Cr2p_{3/2}$ peak (Fig. 3A) was resolved into two peaks with maxima at 576.7 (Cr I) and 579.5 (Cr II) eV, which are attributable to the presence of Cr_2O_3 and CrF_3. The ratio F/Cr II should have been 3 if CrF_3 was formed on the surface, but it was nearly 3.8, indicating that the surface may contain some adsorbed fluorine.

Catalyst B

The BE levels of $Cr2p_{3/2}$, Al2*p*, O1*s*, and F1*s* obtained from the XPS spectrum of catalyst B are given in Table 3. The spectrum obtained for each element was resolved into different components wherever necessary. The as-prepared Cr_2O_3/Al_2O_3 catalyst showed the expected XPS peaks of Al2*p* [74.6 eV], $Cr2p_{3/2}$ [577.0 and 580.0 eV], and O1*s* [531.5 eV]. The BE values of $Cr2p_{3/2}$ levels are higher than those of levels in bulk Cr_2O_3. The shift may be due to interaction with the support (28) and the insulating nature of Al_2O_3, leading to surface charging and line broadening.

The HF-treated sample gave three types of Al in the BE range 74–78 eV, which can arise due to the formation (25–27) of AlF_3, different types of aluminum hydroxyfluorides, and unreacted Al_2O_3. The broad Al2*p* levels obtained were resolved into three peaks. The Al2*p* peak at 74.6 eV was used as internal standard instead of C1*s*. The $Cr2p_{3/2}$ BE values also shift to higher values after treatment with HF due to the formation of chromium hydroxyfluoride and CrF_3. The interpretation of the F1*s* peak is complicated by the presence of both the aluminum oxyfluorides, chromium oxyfluoride, and CrF_3.

The Cr_2O_3/Al_2O_3 sample after fluorination followed by catalytic reaction of TRI with AHF for 24 h was analyzed by

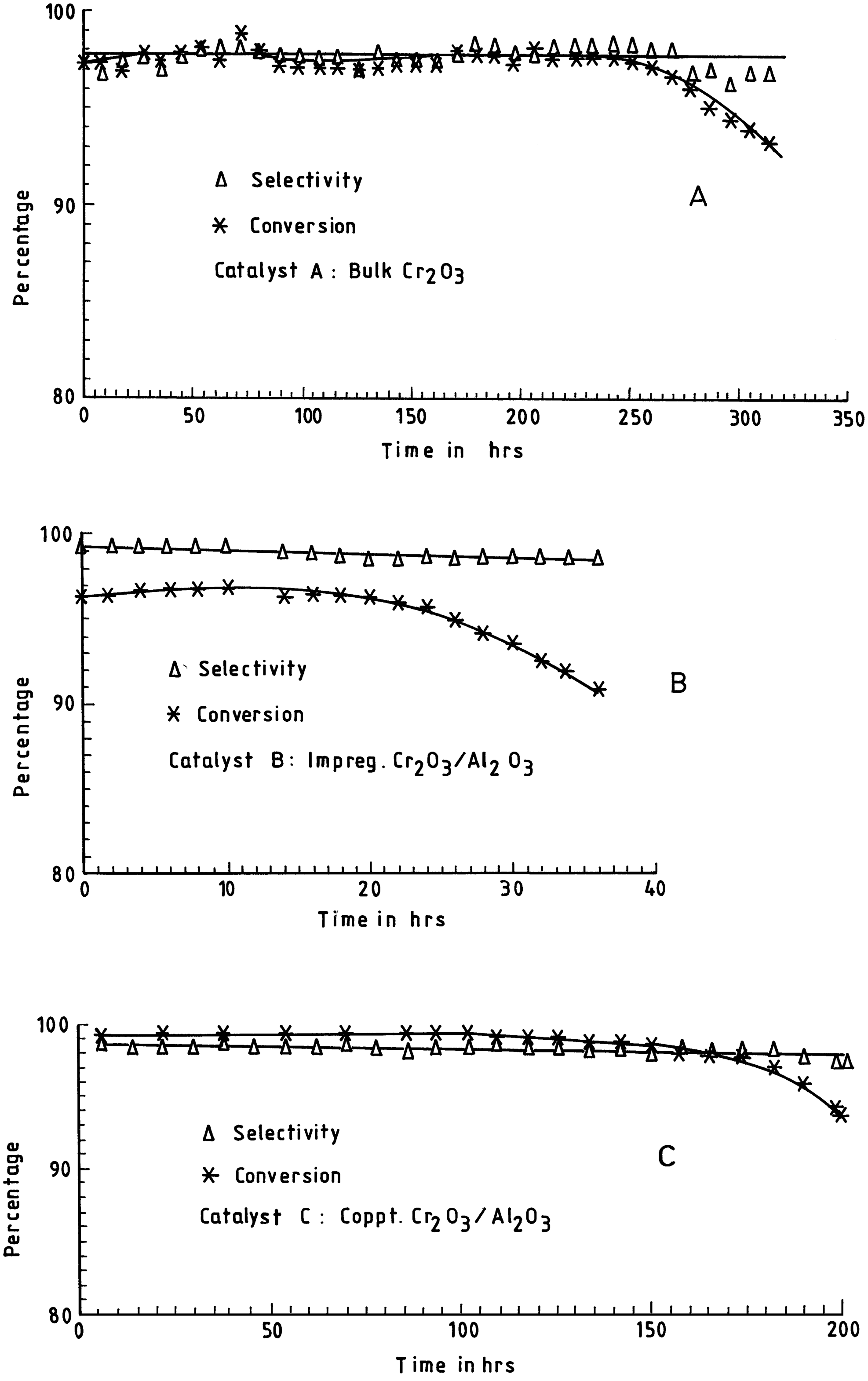

FIG. 4. Time-on-stream analysis of the fluorination of TRI to give HCFC-133a.

TABLE 3

Binding Energy Values for the Cr_2O_3/Al_2O_3 System

	Binding energy (eV)			
Sample	Al2*p*	O1*s*	Cr2$p_{3/2}$	F1*s*
Cr_2O_3/Al_2O_3 (catalyst B)	74.6	531.5	577.0	—
	—	—	580.0	—
Fluorinated Cr_2O_3/Al_2O_3	74.6	532.1	578.3	684.8
	76.1	533.9	580.6	686.5
	77.6	—	—	687.5
After 24 h fluorination reaction of TRI	74.6	530.1	577.1	684.5
	76.8	531.5	580.2	685.8
	78.9	533.8	—	687.7

XPS. Due to the presence of several species on the surface and overlap of their energy levels it is not possible to carry out any meaningful quantitative analysis.

Fluorination of TRI to HCFC-133a

The fluorination of TRI is carried out at 300°C using a mole ratio of HF : TRI (6 : 1) and a contact time of 6 s. We have compared the activity of catalysts A, B, and C in terms of conversion and selectivity. The time-on-stream analysis given in Fig. 4 uses data from after steady state was reached. All three catalysts showed a similar order of activity in terms of conversion and selectivity, but the life exhibited is in the order $Cr_2O_3 >$ co-ppt $Cr_2O_3/Al_2O_3 >$ impregnated Cr_2O_3/Al_2O_3. At this stage we do not have sufficient data to correlate the XPS results with the catalytic activity.

CONCLUSIONS

The ESCA analysis of fluorinated bulk Cr_2O_3 and impregnated Cr_2O_3/Al_2O_3 indicates the formation of fluorine-containing chromium species, which are known to catalyze the halogen-exchange reaction. This species, under the conditions used for fluorination, has been assigned to $Cr(OH)F_2$. The activities of Cr_2O_3 in bulk and supported forms measured in terms of conversions and selectivity in the fluorination of TRI to HCFC-133a were compared. Although all exhibit the same level of activity, the bulk Cr_2O_3 has a longer life than the supported catalysts such as impregnated or coprecipitated Cr_2O_3/Al_2O_3.

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