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Oxidative Destruction of Chlorofluorocarbons (CFC11 and CFC12) by Zeolite Catalysts

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The catalytic oxidations of CFC11 and CFC12 were studied over four Y-zeolite catalysts (H–Y, Co–Y, Ce–Y, and Cr–Y) in a fixed-bed reactor at temperatures ranging from 150 to 400°C and space velocity of 10,500 h^{-1}. Initial oxidation activities and selectivities for each catalyst were measured and compared. Two catalysts (H–Y and Cr–Y) were investigated further at a temperature of 300°C and space velocity of 5000 h^{-1} for longer term stability-deactivation characteristics. Results showed initial activities and selectivities of all four catalysts to be comparatively similar, with substantially complete conversion (>90%) obtained at temperatures ≥250°C for CFC11 and ≥400°C for CFC12. Initial selectivity at higher temperatures (≥250°C) was predominantly to CO_2; F_2 and Cl_2 were largely adsorbed/reacted on the catalysts and could not be quantified. The longer term catalyst deactivation tests carried out on H–Y and Cr–Y showed a drop in catalytic activity and deep oxidation selectivity (partial oxidation products detected were CCl_4, $COCl_2$, and other CFCs) with time due to the deactivation of the catalysts. The Cr–Y catalyst was found to be much more resistant than the H–Y, probably because the Cr^{3+} cations were able to catalyze and subsequently desorb a substantial portion of the corrosive halogens that were formed.

INTRODUCTION

Prior research has shown that chlorofluorocarbon (CFC) emissions are largely responsible for the decline in stratospheric ozone (*1*), which protects the earth by screening out the harmful UV radiation from the sun. Because of this, the general consensus has been to phase out the use of the most harmful CFCs and to manufacture suitable replacement HFCs (hydrofluorocarbons) and HCFCs (hydrochlorofluorocarbons). Safe disposal of the CFCs which are in use now and which are still being produced is equally important. Two alternatives can be proposed: (i) destruction of the small and/or dilute sources of CFCs to form environmentally safe products and (ii) transformation of the large, highly concentrated sources of CFCs to potentially valuable chemical compounds. Some research has been done, mostly in the past 2 to 3 years, in both of the proposed areas.

Aida *et al.* (*2*) have studied the decomposition of CFC12 (CCl_2F_2) over supported gold catalysts; 100% conversion of CFC12 was achieved on an alumina-supported gold catalyst at 500°C. Although decomposition was carried out in the presence of both H_2O and O_2, the authors suggested that hydrolysis of CFC12 was the initiation reaction for its decomposition over these catalysts. No detailed information regarding the selectivity and stability of their catalysts for CFC decomposition was given. Decomposition of CFC12 (CCl_2F_2), CFC13 ($CClF_3$), CFC14 (CF_4), and CFC113 ($CClF_2CCl_2F$) to CO, CO_2, and halogen acids (i.e., HCl and HF) by the reaction with water vapor was studied by Okazaki and Kurosaki (*3*) over various metal oxides and activated-carbon-supported metal oxides. Conversions of over 90% were obtained only on an Fe_2O_3/carbon catalyst at temperatures above 450°C, but

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rapid catalyst deactivation was apparent from the data reported. Imamura *et al.* have studied the oxidative decomposition of CFC12 (CCl_2F_2) on various acid catalysts, such as silica–alumina, titania–silica, and zeolite Y (*4*), and also on a BPO_4 catalyst (*5*). Although good conversions were obtained with many of their catalysts, stability was always a problem, as chlorine and fluorine were retained by, and reacted with, the catalysts.

Selective transformation of CFC113 ($CClF_2CCl_2F$) to different useful compounds has been tried by several researchers. Conversion of CFC113 to chlorotrifluoroethylene ($CClF{=}CF_2$) and to trifluoroethylene ($CHF{=}CF_2$) by selective hydrodechlorination on Bi–Pd catalysts supported on Al_2O_3 and SiO_2 has been studied by Ohnishi *et al.* (*6*); 80–100% conversion was obtained at temperatures between 200–250°C. The authors also suggested further hydrofluorination of trifluoroethylene to form CFC134a (CH_2FCF_3), which has been chosen as a safe replacement of CFC12 for refrigeration. Selective hydrodechlorination of CFC113 has also been studied by Ueda *et al.* (*7*) over supported Ni catalysts and by Takita *et al.* (*8*) over various metal and metal oxide catalysts supported on TiO_2. The catalysts showed good activity but poor stability in the reaction environment.

Catalyst stability has always been a problem of great concern associated with catalytic research involving CFCs. A study of the reactivity of certain CFCs on 13X molecular sieves (which is an alumino-silicate similar to zeolite Y) was carried out earlier by Fevrier *et al.* (*9*); the results showed simultaneous sorption of CFCs on the molecular sieve and reaction of CFCs with the sorbent as well. With prolonged exposure to CFCs, the molecular sieve was irreversibly destroyed, losing its sorption capacity. More recently, Imamura *et al.* (*4*) have reported that their experiments on oxidative decomposition of CFC12 on zeolite Y showed a significant drop in catalyst activity with time as a result of deactivation. Reacting CFCs have been reported to deactivate other catalysts also (*4, 5, 7, 8*), usually within a few hours after exposure.

Although zeolites and cation exchanged zeolites have found diverse applications as catalysts in the process industries, much less consideration has been given to investigating the applicability of cation-exchanged zeolites for the decomposition and/or conversion of CFCs. The present study investigates the suitability of zeolites for the oxidative decomposition of CFC11 and CFC12 and specifically compares the activity and selectivity of three different cation-exchanged zeolites (Co–Y, Ce–Y, and Cr–Y) with that of an H–Y zeolite for the oxidative decomposition of the two CFCs between 150 and 400°C under atmospheric pressure. Calculation shows that decomposition to CO_2, Cl_2, and F_2 is thermodynamically viable at the reaction temperatures used. Deactivation of the zeolite catalysts by the reactive halogens (i.e., chlorine and fluorine) is also investigated.

EXPERIMENTAL

H–Y zeolite pellets ($\frac{1}{16}$ in., LZ–Y62 extrudates) were used as received from Union Carbide Co. to prepare Co–Y, Ce–Y, and Cr–Y catalyst pellets by standard cation-exchange procedures (*10*). The cation exchange of the H–Y pellets was carried out in two steps. In the first step, NH_4^+ exchange of the pellets was performed in NH_4Cl solution. For cation exchanging 100 g of H–Y pellets (on an anhydrous basis), 120.5 g of NH_4Cl (2.23 equivalents) was dissolved in 1000 ml of distilled water. The H–Y pellets were poured into the NH_4Cl solution, and the solution was heated to about 100°C with continuous stirring for about 2 h. The zeolite pellets were then washed with distilled water to remove all soluble salts.

In the second step, metal exchange was carried out by dipping the NH_4^+-exchanged zeolite pellets in an aqueous solution of the corresponding metal nitrate. The amount of metal nitrate used to prepare the solution was such that the total metal content (i.e., Co, Ce, or Cr content) of the nitrate salt used was 3.25 g for 100 g of original anhydrous H–Y pellets. The nitrate salt was dissolved in 300–400 times its weight of distilled water. The salt solution was stirred continuously with a mechanical stirrer and the NH_4^+-exchanged zeolite pellets were slowly poured into the salt solution. Metal exchange was continued over a period of 3 days. After the required time period, the metal-exchanged zeolite pellets were washed thoroughly to remove any soluble salts. The pellets were then dried at 125°C for about 2 h and calcined in air at 500°C over a period of 10–12 h.

After calcination, and before they were subjected to catalyst activity and selectivity experiments, the catalyst pellets were characterized using several analytical techniques. The final metal loadings of the prepared catalyst pellets were obtained using a Philips PV9550 X-ray fluorescence (XRF) spectrometer. The Si/Al ratios of the different zeolite pellets were also determined from the compositional data obtained using the XRF. The percent cation exchange of each exchanged zeolite was calculated based on the corresponding final metal loading, the Si/Al ratio and the unit cell composition of Y zeolite (i.e., $H_{56}(AlO_2)_{56}(SiO_2)_{136}$). The specific surface areas of the catalyst pellets were determined by using a Quantachrome Jr. BET surface area measuring instrument.

Since the activity of a catalyst for oxidative reactions may correlate with the oxygen adsorption capacity of the catalyst, the oxygen adsorption capacities of the different zeolite catalyst pellets were determined at the reaction temperatures using a DuPont Model 2100 Thermal Analyst system with Model 2950 Thermogravimetric Analyzer (TGA).

The compositions, the specific surface areas, and the oxygen adsorption capacities of the catalyst pellets are listed in Table 1. It should be noted that the Si/Al ratio in the H–Y pellets was 1.27, less than the Si/Al ratio for pure Y zeolites (2.43), because an alumina-based binder was used to make these pellets.

Catalyst activity and selectivity experiments along with the deactivation studies were carried out in a vertical Pyrex tubular reactor (31 mm o.d., 27 mm i.d., and 1 m length). A schematic of the reactor is shown in Fig. 1. The reactor had a preheater section for preheating the feed gases and a catalyst section where the reactions took place. For all the experiments, a feed concentration of 1500–2000 ppm of CFC in air was utilized. To feed CFC12 (b.p. −29.8°C) into the reactor, a premixed gas mixture (2% CFC12 in argon, Alphagaz) was diluted with air and used, while a liquid CFC11 bubbler was used to feed CFC11 (b.p. 23.7°C) into the reactor by bubbling air or N_2 through it to vaporize CFC11 for its passage into the reactor. Zeolite catalysts were used in pellet form and were diluted with inert low surface area (0.15–0.35 m^2/g) alumina pellets[2] (8–14 mesh size, obtained from Norton Co.) to form the catalyst bed.

For the catalyst activity and selectivity experiments, 2.85 cc (approximately 1.43 g) of zeolite pellets, mixed with 12.60 cc (15.00 g) of inert alumina pellets, were charged to the reactor. The total gas flow rate through the reactor was ~500 cc/min and the space velocity (based on the volume of active catalyst and reactor entrance conditions, i.e., 23°C and 1 atm) in the catalyst section was ~10,500 h^{-1}. For deactivation studies of the zeolite catalysts, 6.00 cc (~3.00 g) of catalyst pellets were mixed with 12.60 cc (15.00 g) of inert alumina pellets to constitute the catalyst bed. The total gas flow rate through the reactor was maintained at ~500 cc/min, and the space velocity in the catalyst section was ~5000 h^{-1}.

Analysis of the reactor inlet and the effluent gas mixtures was performed using sev-

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[2] Blank reactor runs were carried out with these alumina pellets to confirm their inertness. CFC12 did not show any decomposition up to 500°C, and CFC11 up to 350°C, in an oxidative environment.

TABLE 1

Properties of the Different Fresh Catalysts

Catalyst		H-Y	Co-Y	Ce-Y	Cr-Y
O_2 pickup (mg/g)	T = 225°C	6.11	5.75	3.98	4.39
	T = 250°C	4.64	4.79	3.20	3.93
	T = 300°C	3.06	3.25	2.01	2.15
	T = 450°C	0.167	0.410	0.288	0.665
Surface area (m^2/g)		574.5	576.1	570.5	540.0
Si/Al		1.27	1.30	1.31	1.32
Wt% of	Co	0.00	1.65	0.00	0.00
	Ce	0.00	0.00	2.00	0.00
	Cr	0.00	0.00	0.00	1.32
% Cation exchange			19.0	15.0	20.0

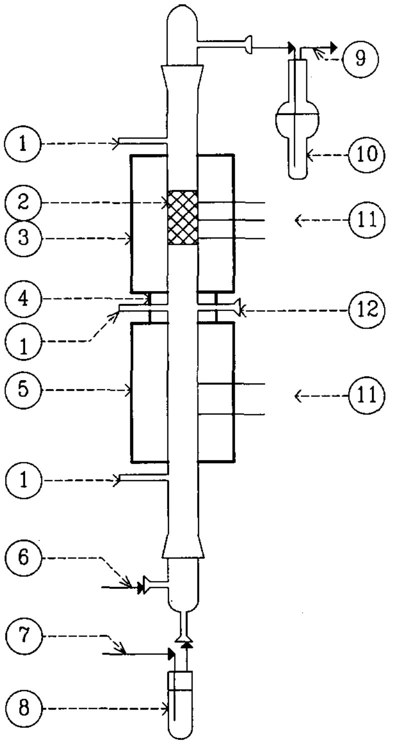

FIG. 1. Schematic of the reactor: (1) sampling ports, (2) catalyst section, (3) reactor furnace, (4) heat tape and insulation, (5) preheater furnace, (6) main air inlet to the reactor, (7) N_2 to the CFC bubbler, (8) CFC bubbler, (9) outlet to vacuum pump, (10) bubbler to trap HCl, HF, etc., (11) thermocouples, and (12) manometer tap.

eral analytical instruments. For the identification and quantification of CFC11, CFC12, CFC13, CFC14, CO_2, and CCl_4, a Hewlett–Packard 5890 GC with a Hewlett–Packard 5970 MS was used. Gas samples from the reactor inlet and the outlet were collected in a Hamilton CR700-200 constant rate syringe and injected into the GC/MS for analysis. Calibration gas mixtures (obtained from Alphagaz and Matheson) with known concentrations of these compounds were also injected into the GC/MS, and the calibration curves obtained were utilized for the quantification of the unknown samples.

Unfortunately, the general purpose fused silica capillary column (Hewlett–Packard Ultra 1) used in the GC was incapable of separating CFC13 ($CClF_3$) and CFC14 (CF_4). Therefore, the small amounts of these gases produced during the deactivation studies could not be quantified separately. In the following text, they are referred to as CFC13/CFC14, and their quantification was performed assuming an equimolar mixture of both the gases.

MSA detector tubes were used for the quantitative detection of Cl_2, CO, and $COCl_2$. To estimate the amount of fluorine (in the molecular form or in the hydracid form) and HCl produced, the reactor effluent was passed through a glass bubbler containing N/20 NaOH solution to trap F_2, HF, Cl_2, HCl, and $COCl_2$. The trap solution was analyzed for the presence of F^- and Cl^- ions using a Corning Model 476042 fluoride electrode and a Model 476126 chloride electrode along with a Corning double junction Model 476370 reference electrode and a Corning Model 255 pH/ion analyzer. The amount of HCl produced was considered to be the difference between the total chloride in the solution and the amount of Cl_2 and $COCl_2$ detected by the MSA detector tubes.

Deactivation studies were carried out only on two of the zeolite catalysts, H–Y and Cr–Y, as these experiments required considerably longer time to perform. It was decided to compare the deactivation characteristics of the Cr–Y pellets with those of the unexchanged H–Y pellets, because the initial activity and selectivity experiments suggested that among the three cation-exchanged zeolites (i.e., Co–Y, Ce–Y, and Cr–Y), Cr–Y was most likely to have maximum resistance against halogen deactivation.

During the deactivation studies, samples from the reactor outlet were injected into the GC/MS every 3–4 min for the first 45–60 min. After 1 h, samples from the reactor outlet were analyzed in the GC/MS every 15–45 min. All the deactivation studies were carried out at 300°C for a total of ~7 h. Detector tubes were not used for the monitoring the Cl_2 and $COCl_2$ during the deactivation studies. $COCl_2$ was quantified (based on an approximate calibration) using the GC/MS, and $Cl_2$was monitored qualitatively using an online Ametek Dycor Residual Gas Analyzer (RGA). Continuous monitoring of fluorine (F_2 and/or HF) and HCl was not possible using the ion selective electrodes, and, therefore, they could not be determined during the deactivation studies.

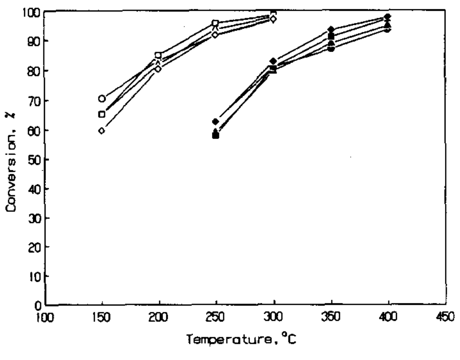

FIG. 2. Conversion of CFC11 and CFC12 vs temperature (space velocity = 10500 h^{-1}): ○, H–Y/CFC11; △, Co–Y/CFC11; ◇, Ce–Y/CFC11; □, Cr–Y/CFC11; ●, H–Y/CFC12; ▲, Co–Y/CFC12; ◆, Ce–Y/CFC12; ■, Cr–Y/CFC12.

RESULTS

I. Initial Activity and Selectivity Studies[3]

Initial activity. The initial activities of the four catalysts (H–Y, Co–Y, Ce–Y, and Cr–Y) for the CFC11 and the CFC12 feeds are compared in Fig. 2. At a space velocity of 10,500 h^{-1}, conversion of CFC11 on all four catalysts reached ≥90% at a much lower temperature (250°C) compared to CFC12, which attained ≥90% conversion only at 400°C and above. At 250°C, conversion of CFC12 was only 55–65%. No significant differences in initial activity among the four catalysts tested could be noted for either feed.

However, it could be noted from Table 2 (and Fig. 2 as well) that the drop in conversion for both the feeds from the highest reaction temperature to the lowest reaction temperature was minimum for the H–Y catalyst. Conversions at the highest reaction temperatures of 300°C for CFC11 and 400°C for CFC12 (which were the first experiments carried out in each set) were always slightly lower on H–Y than on the Co–Y, Ce–Y, or Cr–Y catalysts for both the feeds (for CFC11: 96.8, 98.0, 97.2, and 98.4%, respec-

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[3] The same catalyst was used for each of four initial activity/selectivity runs as shown in Table 2. Since catalyst deactivation can be fairly rapid, as discussed later, the terms "initial activity" and/or "initial selectivity" as applied to catalyst with prior exposure history of from 22–88 min may generate slight error in these values.

TABLE 2

Compilation of Results

Run	Temp (°C)	Feed	Conversion (%)	Selectivity to CO + CO_2 (%)	Ratio CO_2/CO	Ratio HCl/Cl_2
H–Y						
268	300	CFC11	96.8	86.7	a	a
269	250	CFC11	91.6	58.0	a	a
270	200	CFC11	83.0	17.3	a	a
271	150	CFC11	70.6	0.0	b	b
294	400	CFC12	93.7	100.0	a	111.2
295	350	CFC12	87.0	98.7	a	a
296	300	CFC12	80.9	93.1	a	a
297	250	CFC12	63.0	79.1	a	a
Co–Y						
264	300	CFC11	98.0	79.9	3.21	25.44
265	250	CFC11	93.7	37.3	2.36	19.44
266	200	CFC11	81.8	2.7	a	16.67
267	150	CFC11	65.4	0.4	a	b
298	400	CFC12	94.9	98.9	6.57	60.05
299	350	CFC12	88.8	96.3	6.65	18.09
300	300	CFC12	79.7	84.4	6.71	20.69
301	250	CFC12	58.8	60.9	7.41	42.18
Ce–Y						
272	300	CFC11	97.2	75.5	a	43.06
273	250	CFC11	91.8	32.8	a	32.91
262	200	CFC11	80.4	3.3	a	35.0
263	150	CFC11	59.8	2.0	a	4.0
302	400	CFC12	97.8	99.7	a	14.26
303	350	CFC12	93.3	86.1	a	23.67
304	300	CFC12	82.8	70.7	a	43.17
305	250	CFC12	62.7	43.7	a	117.33
Cr–Y						
274	300	CFC11	98.4	94.8	a	2.59
275	250	CFC11	95.7	68.6	a	2.18
276	200	CFC11	85.0	15.3	a	6.76
277	150	CFC11	65.3	2.6	a	b
306	400	CFC12	97.3	100.0	a	1.18
307	350	CFC12	90.9	100.0	a	1.91
308	300	CFC12	80.9	95.0	a	1.54
309	250	CFC12	57.9	92.7	a	2.06

Note. Space velocity = 10,500 h^{-1}; a, denominator is zero; b, both numerator and denominator are zero.

tively, and for CFC12: 93.7, 94.9, 97.8, and 97.3%, respectively). Conversely, the conversions at the minimum reaction temperatures of 150°C for CFC11 and 250°C for CFC12 (which were the last experiments carried out in each set) were always higher on the H–Y than on the cation exchanged Y zeolites for either feed (for CFC11: 70.6, 65.4, 59.8, and 65.3%, respectively, and for CFC12: 63.0, 58.8, 62.7, and 57.9%, respectively). The reason for this initial activity behavior with temperature over H–Y is discussed later.

Initial selectivity. Although no significant differences in activity of the fresh catalysts were observed, some differences in initial selectivity among the four Y-zeolite catalysts could be noted; results are tabulated in Table 2.[4] The products detected in the reactor effluent were CO_2, CO, $COCl_2$, CCl_4, Cl_2, and HCl. Small quantities of CFCs (CFC11 from CFC12 feed and CFC12 from CFC11 feed) were also detected at lower temperatures. CO was detected only during the Co–Y experiments. Selectivity to CO_2 (CO + CO_2 in the case of Co–Y) was highest for the Cr–Y catalyst, decreasing in the following order: Cr–Y > H–Y > Co–Y > Ce–Y, for both the feeds. Selectivity to CO and CO_2 also decreased with decreasing reaction temperature for all the catalysts.

Selectivity to Cl_2 was highest for the Cr–Y catalyst, while almost no Cl_2 was detected for the other three catalysts. Selectivity to Cl_2 decreased in the following order: Cr–Y > Co–Y ≃ Ce–Y > H–Y. Although no water was added to the feed, large amounts of HCl were detected in the effluent during the experiments with both the feeds. Since the Cr–Y catalyst produced considerable Cl_2, the HCl produced from the Cr–Y catalyst was correspondingly less compared to the other three catalysts at all temperatures. Some experiments, especially the first one or two experiments of any set, showed poor chlorine balances (chlorine balances varied from 60–100%). No F_2 or HF were detected in any product streams.

II. Deactivation Studies

As mentioned earlier, deactivation studies were carried out only on two zeolite catalysts, H–Y and Cr–Y. In a preliminary attempt to predict which zeolite-based catalysts would be more resistant to halogen deactivation, it was reasoned that chlorine and fluorine produced during the combustion of CFCs could either be retained by the zeolite pellets (perhaps in the form of AlF_3 and/or $AlCl_3$) or that they could be reacted with the acidic H^+ sites to form halogen acids. It was observed that appreciable amounts of chlorine and some HCl were released only from the Cr–Y pellets. Based on this observation, it was expected that Cr–Y pellets would have better resistance against halogen deactivation compared to H–Y pellets or the other cation-exchanged pellets (i.e., Co–Y and Ce–Y). Therefore, it was decided to compare the deactivation characteristics of the Cr–Y catalyst with that of the H form of the Y zeolite. The deactivation studies carried out for 7 h proved that the cation exchange of the H–Y pellets with Cr^{3+} did indeed improve the stability of the Y-zeolite pellets against halogen deactivation.

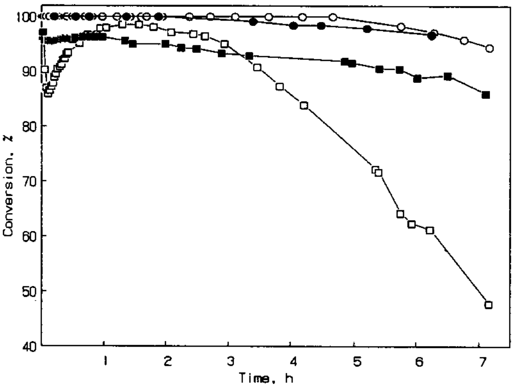

FIG. 3. Deactivation of H–Y and Cr–Y for CFC11 and CFC12 feeds at 300°C (space velocity = 5000 h^{-1}): ○, H–Y/CFC11; □, H–Y/CFC12; ●, Cr–Y/CFC11; ■, Cr–Y/CFC12.

Activity vs time. Figure 3 compares the deactivation effects of CFC11 and CFC12 feeds on their conversions over the H–Y and the Cr–Y catalysts at 300°C and a space velocity of 5000 h^{-1}. It can be noted that the initial behavior of CFC12 conversion on H–Y pellets is drastically different from that on Cr–Y pellets. For the H–Y pellets, the observed conversion first decreased, reach-

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[4] Selectivities reported in Table 2 were calculated as follows: For determining the selectivity to CO_2 (CO + CO_2 in the case of Co–Y), the concentration of CO_2 in the effluent (or CO + CO_2) was divided by the sum of the concentrations of all the carbon-containing products, such as CO_2, CO, CCl_4, $COCl_2$, etc. Similarly, for determining the selectivity to HCl and/or Cl_2, the concentration of each was divided by the sum of the concentrations of all the chlorine-containing products, such as HCl, Cl_2, CCl_4, $COCl_2$, etc.

ing a minimum of ~85% after ~0.05–0.07 h (i.e., ~3–4 min), before starting to increase again. It increased sharply for ~0.5 h and then more slowly for ~0.5 additional hour, reaching a maximum of 97–99% conversion after about 1 h. This initial trend in the conversion of CFC12 on the H–Y pellets was not found on the Cr–Y pellets. Although an initial drop in CFC12 conversion (from ~97% to ~95%) on the Cr–Y catalyst could be noted, no subsequent increase in conversion was noticeable. This initial drop followed by subsequent increase in conversion was also not observed with the CFC11 feed on either of the catalysts.

It can also be noted from Fig. 3 that after ~1 h of reaction time, conversions of CFC12 on both H–Y and Cr–Y pellets remained between 95 and 97%. However, after ~3 h, conversion on H–Y began to deteriorate, such that after ~7 h, conversion on Cr–Y was much higher (~87%) compared to that on H–Y (~50%). Conversion of CFC12 on Cr–Y pellets dropped slowly and steadily over the 7 h period, while on H–Y pellets it dropped slowly for the first 2.5–3 h and rapidly after that.

Figure 3 also shows that the small drop in conversion of the CFC11 feed was the same for both the catalysts during the experimental period. The initial conversion of CFC11 was 100% on both the catalysts, whereas, after ~6.5 h it had decreased slightly to ~96–97% on both the catalysts. Thus, the deactivation after ~7 h was much greater with the CFC12 feed (conversion loss of ~10% on Cr–Y and ~50% on H–Y) compared to CFC11 feed (conversion loss of ~3–4% on both Cr–Y and H–Y).

Selectivity vs time. Figure 4 shows that the initial deep oxidation selectivity of the H–Y catalyst for the decomposition of CFC12 feed was very high, with 100% selectivity to CO_2. However, selectivity to CO_2 dropped with time, probably due to catalyst deactivation. With the decrease in selectivity to CO_2, it can be seen from Fig. 4, that the selectivity toward $COCl_2$, CCl_4 and CFC11 increased greatly with time.

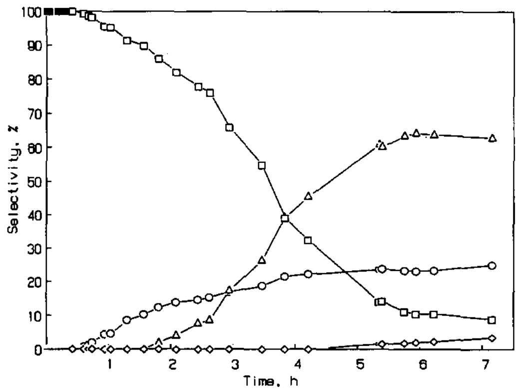

FIG. 4. Selectivity of H–Y with time for CFC12 feed at 300°C (space velocity = 5000 h^{-1}): □, CO_2; ○, $COCl_2$; △, CCl_4; ◇, CFC11.

Figure 5 shows the change in selectivity with time for the Cr–Y catalyst during CFC12 decomposition. Initial conversion of CFC12 was 100% selective to CO_2 on the Cr–Y catalyst also. With time, selectivity changed modestly, producing measurable quantities of $COCl_2$, CCl_4, CFC11, CFC13/CFC14, and Cl_2.

Figure 6 describes how the selectivity of H–Y for CFC11 decomposition changed with time due to catalyst deactivation. Besides CO_2, the halogenated products detected during oxidation of CFC11 on H–Y were $COCl_2$, CCl_4, and CFC12. It is appar-

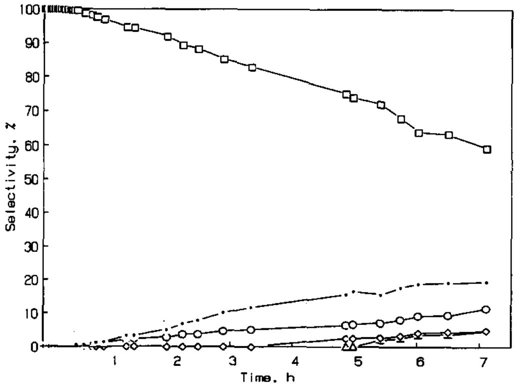

FIG. 5. Selectivity of Cr–Y with time for CFC12 feed at 300°C (space velocity = 5000 h^{-1}): □, CO_2; ○, $COCl_2$; △, CCl_4; ◇, CFC11; ·, CFC13/CFC14.

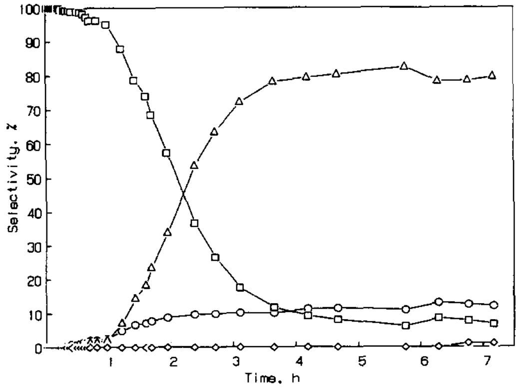

FIG. 6. Selectivity of H–Y with time for CFC11 feed at 300°C (space velocity = 5000 h^{-1}): □, CO_2; ○, $COCl_2$; △, CCl_4; ◇, CFC12.

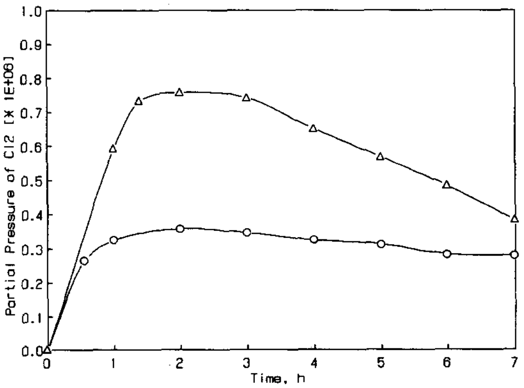

FIG. 8. RGA response for Cl_2 in the effluent during Cr–Y deactivation (space velocity = 5000 h^{-1}): △, CFC11 feed; ○, CFC12 feed.

ent from Fig. 6 that the initial deep oxidation selectivity (i.e., 100% selective to CO_2) of the H–Y catalyst deteriorated with time due to catalyst deactivation.

Similarly, from Fig. 7, it can be noted that the initial selectivity of the Cr–Y catalyst for the oxidative decomposition of the CFC11 feed was 100% to CO_2, which gradually decreased with time corresponding to the increase in the selectivities to the other halocarbon products.

Although no chlorine was detected during the deactivation experiments of the H–Y pellets, as mentioned earlier, chlorine was detected during the Cr–Y deactivation experiments. RGA responses (uncalibrated) for Cl_2 in the reactor effluent during the Cr–Y deactivation studies are plotted in Fig. 8. Cl_2 concentration in the effluent steadily increased from zero to a maximum concentration over a period of ~1–1.5 h, while during the next few hours, it dropped slowly. Also the concentration of chlorine produced at any time was ~1.5–2 times higher in the case of CFC11 feed than in the case of CFC12 feed. As mentioned earlier, HCl could not be monitored during the deactivation studies.

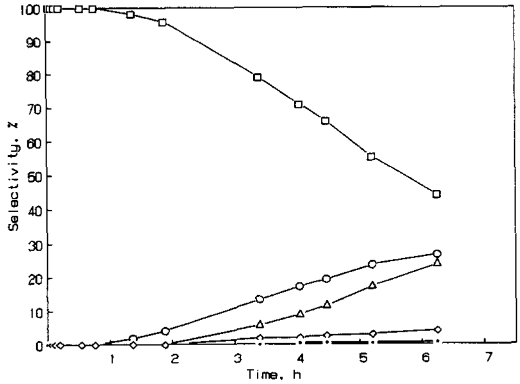

FIG. 7. Selectivity of Cr–Y with time for CFC11 feed at 300°C (space velocity = 5000 h^{-1}): □, CO_2; ○, $COCl_2$; △, CCl_4; ◇, CFC12; ·, CFC13/CFC14.

H–Y vs Cr–Y selectivity for CFC12 feed. Comparison of Figs. 4 and 5 reveals that the overall drop in CO_2 selectivity during CFC12 deactivation was more pronounced in the case of H–Y pellets (from 100% down to ~10%) than in the case of Cr–Y pellets (from 100% down to ~60%). The overall increase in selectivities to the other halogenated products was also greater on the H–Y pellets than on the Cr–Y pellets. With time, the selectivity to CCl_4 increased from 0 to ~63% on the H–Y catalyst and from 0 to only 4–5% on the Cr–Y catalyst. Selectivity to $COCl_2$ increased from 0 to ~25% on the H–Y catalyst, while on Cr–Y catalyst it increased from 0 to ~11%. Selectivity to CFC11 was about the same (a maximum of

~5%) on both the catalysts. CFC13/CFC14 species were formed only on the Cr–Y catalyst; they were not detected during the deactivation run for the H–Y catalyst.

H–Y vs Cr–Y selectivity for CFC11 feed. Comparing Figs. 6 and 7, it can be seen that also during the deactivation study of the CFC11 feed, selectivity to CO_2 dropped on both the H–Y and the Cr–Y catalysts. The drop was more in the case of H–Y pellets (from 100% down to ~8%) than in the case of Cr–Y pellets (from 100 down to ~42%). Selectivities for the halocarbon products increased with time and the overall increase (especially for CCl_4) was much greater during the deactivation of the H–Y pellets. Selectivity to CFC12 was slightly larger on the Cr–Y catalyst (a maximum of ~5%) than on the H–Y catalyst (1–2%). No CFC13/CFC14 species were detected during the deactivation study of the H–Y catalyst with the CFC11 feed also.

XRD analyses of the deactivated catalysts indicated partial destruction of the zeolite crystal structure. Surface area and oxygen pickup analyses of the deactivated catalysts also showed a drop in those values. A more detailed comparative study is in progress now.

DISCUSSION

I. Initial Activity and Selectivity Studies

Initial activity. As illustrated in Fig. 2, conversion of CFC11 at any temperature was higher than that of CFC12, probably since CFC11 is less stable compared to CFC12 due to the presence of only one fluorine atom in its molecule as compared to two in CFC12 (the C–F bond is much stronger, with a bond energy of 105.4 kcal/mole, compared to the C–Cl bond, with a bond energy of 78.5 kcal/mole).

The initial activities, as observed in Fig. 2, of the cation-exchanged Co–Y, Ce–Y, and Cr–Y zeolites for the oxidative destruction of CFC11 and CFC12 were not significantly different from that of the H–Y zeolite, probably because the percent cation exchange (listed in Table 1) of the cation-exchanged zeolites was rather small (for example, Ca–Y has been reported to have significant activity for the alkylation of benzene with propylene only beyond 25% exchange (11)). During calcination of a cation-exchanged zeolite, it has been reported that the multivalent cations move preferentially to the type I sites located inside the hexagonal prisms and the type I′ and II′ sites located inside the sodalite cages, as it is easier for the multivalent cations to neutralize the negative charges on the closely spaced framework aluminum atoms located inside the smaller hexagonal prisms and the sodalite cages (*12, 13*). As a result, the modest degree of H^+ exchange with multivalent cations (such as in the present case with Co^{2+}, Ce^{3+}, and Cr^{3+}) may not have been sufficient to cause significant differences in catalytic activity, as many of the cations were located inside the small hexagonal prisms and the sodalite cages and could not be accessed by the feed molecules. As an alternate explanation it could also be possible that, irrespective of the exchange levels in the cation-exchanged zeolites, the H–Y zeolite was an equally good catalyst for the destruction of CFC11 and CFC12.

It should also be pointed out that the oxygen pickup capacities of the zeolite catalysts did not appear to control the activities of the catalysts, as significant differences in the O_2 pickup values, as listed in Table 1, were observed with no corresponding trend in activity.

The experiments listed in Table 2 were carried out starting with fresh catalyst in the order of decreasing temperature. At the highest temperature, conversions of CFC11 and CFC12 on the H–Y catalyst were slightly lower as compared to the metal-exchanged Y zeolites. Conversely, the conversions at the lowest temperature were slightly higher on the H–Y, which suggested gradual improvement in the activity of the H–Y catalyst during the initial reaction time. One explanation for this is that zeolites undergo dealumination (i.e., partial removal of alumina from the structure through mild fluorination (*14–16*)). Thus, the total number of acidic sites is reduced but the strength of the remaining isolated acidic sites increases (*17*), which would be manifested as an increased activity for acid-catalyzed reactions. On the contrary, Becker and Kowalak (*16*) demonstrated that fluorination of a cation-exchanged Y zeolite does not generate acidic sites stronger than those that existed before fluorination. Therefore it is possible that H–Y showed gradual increase in activity over the cation-exchanged zeolites due to opposing effects of mild fluorination on these catalysts by the CFC feeds. This phenomenon was more prominent during the deactivation studies, as discussed later.

Initial selectivity. The differences in selectivity, as listed in Table 2, among the four zeolite catalysts suggested that at least some of the exchanged cations in the cation-exchanged zeolites were located inside the supercages and could be accessed by the feed molecules and the reaction intermediates. It is also possible that the small molecules and radicals formed during the decomposition of CFC11 and CFC12, such as HF, F·, and O·, were able to access the exchanged cations located inside the sodalite cages, thereby influencing the selectivity of the catalysts.

The drop in CO_2 selectivity (both CO and CO_2 in the case of Co–Y) with decreasing temperature was perhaps a combined effect of decreasing temperature and progressive early deactivation of the catalysts. Products such as CCl_4 and $COCl_2$ were produced at lower temperatures, but with increasing temperature they were further oxidized to CO and CO_2, which suggested a series reaction in which CCl_4 and/or $COCl_2$ were produced as reaction intermediates. The oxidation reaction probably followed a slightly different path on Co–Y, producing some amount of CO. Unlike the other three catalysts, Cr–Y produced considerable chlorine owing to the presence of Cr^{3+}, which is well known as a Deacon catalyst.

Although no hydrogen source was added to the feed, substantial HCl was detected in the reactor effluent, especially for H–Y, Co–Y, and Ce–Y catalysts. In this case, the constitutional water molecules in the zeolite most likely reacted with chlorine yielding HCl. No F_2 or HF were detected in the product stream, probably because fluorine was retained by the catalyst. This result agrees with Imamura *et al.* (*4*) who have reported that ESCA analysis of their catalysts showed the presence of fluorine. XRF analysis of our catalysts indicated the presence of chlorine in the catalysts after the reactor runs. Unfortunately the instrument was not capable of detecting any element below sodium in the periodic table and thus could not detect fluorine. The retention of fluorine by the zeolite catalysts could then cause gradual deactivation of them, as discussed in detail in the next section.

II. Deactivation Studies

The complete oxidation products for CFCs which have no hydrogen atom in them are CO_2, Cl_2, and F_2. They can be formed typically as follows:

$$\text{CFC11 } (CCl_3F) + O_2 \rightarrow CO_2 + \tfrac{3}{2}Cl_2 + \tfrac{1}{2}F_2$$

$$\text{CFC12 } (CCl_2F_2) + O_2 \rightarrow CO_2 + Cl_2 + F_2.$$

F_2 is the most electronegative and chemically reactive element in the periodic table, reacting with almost any metal or nonmetal. As no F_2 or HF were detected in the product stream, it is probable that fluorine and any HF produced from the reaction between F_2 and zeolitic water, reacted with the structural silica–alumina of the zeolite catalyst and caused much of the deactivation during the oxidative decomposition of CFCs.

Activity vs time. As observed in Fig. 3, the initial drop in CFC12 conversion (for the first 3–4 min) on the H–Y catalyst was probably due to the reactor residence time and also due to the initial adsorption of CFC12 and reaction products on the catalyst surface before reaching equilibrium. Depending on the flow rate through the reactor, the reactor dimensions, and also the initial adsorption of CFC12 on the catalyst surface, the feed CFC12 molecules took some time (~1 min, excluding initial adsorption effect) to reach the reactor top and, therefore, an initial high "conversion" was observed due to the absence of any CFC12 molecules at the reactor exit. After the initial drop, conversion of CFC12 again increased probably due to the mild fluorination and the simultaneous increase in acidity of the H–Y catalyst, as explained earlier.

This initial trend was not observed with the CFC11 feed (Fig. 3), probably because CFC11 was more reactive than CFC12 (only one fluorine atom compared to two in CFC12, and C–F bonds are stronger than C–Cl bonds) and was easier to destroy. Therefore, conversion of CFC11 at 300°C remained at 100% with time even on the unaltered H–Y surface.

As also demonstrated in Fig. 3, the more rapid decrease in CFC12 conversion with time on the H–Y catalyst than on the Cr–Y catalyst suggests lesser deactivation of the latter. Several theories could be postulated to reason why Cr–Y catalyst was less deactivated. Since hydrocarbon molecules are believed to adsorb on the acidic H^+ sites of the zeolites, it is possible that CFC molecules were likewise also adsorbed on H^+ sites and, after interacting with adsorbed oxygen, produced CO_2 molecules which left the surface, while the adsorbed Cl · and F · (or a fraction of them) remained on the surface. The adsorbed Cl · and F · could then bond with acidic sites forming halogen acids, or could react with an adjacent alumina, silica, or chromia (in the case of Cr–Y), forming the respective metal halides by replacing lattice oxygens. In both cases, the zeolite crystal structure would be destroyed either due to the very low pH environment or due to the replacement of lattice oxygen. Formation of HF on the surface could also cause reaction of HF with crystalline silica to form volatile SiF_4. Production of considerable chlorine in the case of Cr–Y (Fig. 8) could be due to Cr^{3+}, which is a good Deacon catalyst. It is possible that any F_2 formed was partially released from the Cr–Y surface too, but was later adsorbed on the surface of the glass reactor. As H–Y did not show any halogens in the product stream, loss of constitutional water in the form of HCl (and therefore acidity) and perhaps replacement of lattice oxygen by the surface adsorbed halogens was greater compared to Cr–Y, which perhaps resulted in the increased deactivation of the H–Y catalyst.

In the case of Cr–Y, the total number of H^+ sites is probably much lower compared to H–Y, as a fraction of the protons had previously been exchanged with Cr^{3+}. Therefore the probability for the formation of HF and HCl during initial runs was much less. This was also perhaps one of the reasons why Cr–Y showed less deactivation compared to H–Y.

As shown in Fig. 3, the drop in CFC11 conversion was nearly the same on both the H–Y and the Cr–Y catalysts for the 6.5 h duration of the deactivation runs. Differences probably would have been noted only if the deactivation study had been continued for a longer time. However, the deactivation of the catalysts during CFC11 oxidation was apparent from the changes in selectivities to the various products as shown in Figs. 6 and 7, and subsequently discussed.

The XRD analysis of the catalysts carried out both before and after the deactivation studies also indicated partial destruction of the zeolite crystalline structure during reaction. Surface areas and oxygen pickup capacities of the catalysts were also reduced due to deactivation. No data are provided since a detailed comparative structural study has yet to be performed.

Selectivity vs time. For both the catalysts, and with both of the feeds, the selectivity to higher chlorinated and fluorinated products increased with time, with the simultaneous decrease in the selectivity to CO_2. This phenomenon could be explained by noting that the destruction of the zeolite crystalline structure probably produced amorphous silica and alumina or even halides of aluminum (i.e., AlF_3 and $AlCl_3$; halides of Si would evaporate at the reaction temperature), resulting in significant changes in the physical nature of the catalyst and also catalyst selectivity. The fairly high conversions but poor deep oxidation selectivities (i.e., not selective to CO_2) at the end of the deactivation studies are indicative of the fact that porous zeolite crystalline structures were destroyed. As the deactivation and perhaps the consequential destruction of the crystal structure were greater in the case of H–Y catalyst, the increase in halocarbon selectivity and the decrease in CO_2 selectivity were also higher for this catalyst.

Detection of CFC13/CFC14 (Figs. 5 and 7) in the case of the Cr–Y catalyst indicated partial use of fluorine to form higher fluorinated products, thereby resulting in lesser deactivation of this catalyst from fluorine as compared to H–Y.

The observed deactivation of the zeolite catalysts was probably more pronounced with the CFC12 feed than with the CFC11 feed for several reasons. First, CFC12 contains twice the fluorine atoms of CFC11 which can form corrosive products. Second, CFC11 is more reactive and could remain at full conversion even though some sites had already been destroyed.

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