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An Investigation of CFC12 (CCl_2F_2) Decomposition on TiO_2 Catalyst

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The catalytic oxidation of CFC12 was studied over a titania (TiO_2) catalyst in a fixed-bed reactor at temperatures ranging from 200 to 400°C and space velocity of 10,500 h^{-1}. Results showed substantially complete conversion of CFC12 (>90%) to CO_2 and halogen acids at and above 300°C. Longer term deactivation studies carried out in the presence of water vapor as a cofeed at 300°C showed less than 5% change in activity and selectivity of the titania catalyst even after 4 days of operation. Nevertheless, a 75% reduction in catalyst surface area was observed after 4 days, most of which (50%) took place during the initial 1–1.5 h of reaction. Despite the 50% drop in surface area, the activity of the titania catalyst increased during the initial 1–1.5 h. Results of various experiments indicated that the increased activity of the catalyst was brought about by an increase in surface acidity due to surface fluorination. *In situ* FTIR techniques were employed to study the reaction mechanism of CFC12 destruction on the titania catalyst. Results indicated adsorption of CFC12 on the surface hydroxyls with further reaction between adsorbed CFC12 and surface hydroxyls leading to the formation of complete oxidation products through COFCl and $COCl_2$ intermediates. © 1995 Academic Press, Inc.

INTRODUCTION

Recent scientific studies have shown a striking correlation between stratospheric ozone depletion and chlorofluorocarbon (CFC) emissions (1). Ozone in the stratosphere is essential for survival of life on earth since it absorbs biologically harmful solar ultraviolet radiation. Today, the general consensus is to phase out the use of the most harmful CFCs and to manufacture suitable replacement HFCs (hydrofluorocarbons) and HCFCs (hydrochlorofluorocarbons). Safe disposal of the enormous volumes of CFCs which are in use now and which are still being produced is equally important. Catalytic destruction of CFCs using Y zeolite catalysts was studied earlier by us; however, the deactivation process was rather rapid (2, 3). Therefore, experiments continued with various other catalysts such as metal fluorides and oxides. Among the catalysts studied, titania (TiO_2) had the maximum activity as well as stability for the oxidative destruction of both CFC11 and CFC12 (4). This paper discusses the activity, selectivity, stability, and destruction mechanism of CFC12 on the titania catalyst.

Some research has been done, mostly in the past 3 to 4 years, to explore the applicability of catalysts for the destruction of CFCs. Aida *et al.* (5) have studied the decomposition of CFC12 over supported gold catalysts; 100% conversion of CFC12 was achieved on an alumina-supported gold catalyst at 500°C. The authors chose gold as the catalyst because, due to its chemical inertness, they expected to avoid possible catalyst degradation caused by highly corrosive reaction products. However, no data supporting the stability of the catalyst were reported. Decomposition of CFC12, CFC13, CFC14, and CFC113 to CO, CO_2, HCl, and HF by the reaction with water vapor was studied by Okazaki and Kurosaki (6) over various metal oxides and activated carbon-supported metal oxides. Conversions over 90% were obtained only on an Fe_2O_3/carbon catalyst at temperatures above 450°C. Although the enigma of catalyst deactivation was not discussed in particular, rapid catalyst deactivation was apparent from the data reported. Imamura *et al.* have studied the oxidative decomposition of CFC12 on various acid catalysts, such as silica–alumina, titania–silica, and zeolite Y (7), and also on a BPO_4 catalyst (8). The titania–silica catalyst containing 60 mole% Ti exhibited the best performance among the acid catalysts investigated with >90% conversion at a space velocity of 5900 h^{-1} at and above 500°C. The activity of the catalyst, however, dropped sharply within 150 min, and only 10% CFC12 was decomposed after 10 h. The authors suggested that silicon in the catalyst reacted with fluorine, and the fine TiO_2 crystal that was surrounded by SiO_2 aggregated to form large TiO_2 grains. The authors acknowledged the necessity of investigating the effect of the presence of additional water or other organics in the feed on the stability of their catalysts. Decomposition of CFC112 and CFC113 in the presence of ethanol was studied by Miyatani *et al.* (9). Reactions were carried out on an $FeCl_3$ catalyst supported on activated charcoal in a flow type reactor with a CFC-to-ethanol molar ratio of 1 : 4. Besides CO and CO_2, various partial oxidation products were

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detected, especially at lower temperatures, from the decomposition of CFCs.

A few patents (10–13) have also been published in recent years describing the application of noble metal or metal oxide catalysts for heterogeneous oxidative destruction of CFCs. A sulfated CuO/TiO_2 catalyst was used by Jacob (10) to decompose CFCs in the presence of water vapor and optionally oxygen to form CO_2 and hydrogen halides. More than 90% conversions of single-carbon and two-carbon CFCs were obtained at temperatures between 300 and 500°C and at a reactor residence time of 2 sec. Imoto *et al.* (11) have demonstrated >99% decomposition of 500 ppm of CFC113 in air at a temperature of 500°C and a space velocity of 2500 h^{-1}. The composition of their patented catalyst covered a wide range of metals and metal oxides comprising metals or oxides of the metals Pt, Rh, Pd, Ru, Mn, Cu, Cr, and Fe, and oxides of Zr, Ti, Al, W, and Si. Very high catalytic activity of a catalyst material consisting of metals selected from the groups containing Ti, Zr, Nb, Ni, and Co or an alloy consisting of at least two elements, one from the group consisting of Ni and Co and another from the group consisting of Ti, Zr, and Nb, has been illustrated by Hashimoto *et al.* (12) for the decomposition of CFC12. The decomposition reaction was carried out in the presence of water, but oxygen was not added. Although the metallic catalyst components were converted into fluorides over time, catalyst activity was reportedly retained during the decomposition process. Hashimoto and Habazaki (13) have also demonstrated high activity of an amorphous alloy type catalyst for the decomposition of CFC12 in the presence of water vapor. The catalyst consisted of elements from the groups containing Ti, Zr, Nb, and Co and also at least one element from the precious metal group, i.e., Ru, Rh, Pd, Ir, and Pt.

Although TiO_2 has been studied in a mixture with various other metals and/or metal oxides, properties of this transition metal oxide as an individual catalyst for CFC destruction are not found in the literature. The present study investigates the applicability of titania for the oxidative decomposition of CFC12 between 200 and 400°C under atmospheric pressure. Detailed studies were also carried out to investigate the stability of the titania catalyst under reacting conditions. Finally, *in situ* FTIR techniques were employed to study the reaction mechanism of CFC12 destruction on the titania catalyst.

EXPERIMENTAL

The titania catalyst used in this study was received from Norton Co. in the form of 1/8-inch extrudates and had an anatase-type crystalline phase. XRD analysis carried out in our laboratory also confirmed the anatase phase of the sample. The extrudates were crushed and sieved to 12–14 mesh size for the catalyst reactor experiments that were carried out to determine the initial activity, initial selectivity, and stability of the TiO_2 catalyst.

The reactor experiments were carried out in a vertical Pyrex tubular reactor, a schematic of which has been shown elsewhere (2). The reactor had a preheater section for preheating the feed gases and a fixed-bed catalyst section where the reactions took place. Experiments were carried out with and without water vapor in the feed as described below:

1. CFC12 feed (1500–2000 ppm) with excess oxygen (20% in air), and
2. CFC12 feed (1500–2000 ppm) and H_2O (5000–6000 ppm) with excess oxygen (20% in air).

Analysis of the reactor inlet and effluent gas mixtures was performed using a HP 5890 GC with a HP 5970 MS. Calibration gas standards were also injected into the GC/MS to quantify the amounts of CFCs, CO_2, CCl_4, etc. in the reactor inlet and outlet streams as well. Details of the analytical techniques involved in the reactor experiments are discussed elsewhere (2, 4).

In situ FTIR experiments were carried out to study the surface of the catalyst and any reaction intermediates formed during CFC12 oxidation on the titania catalyst. A Bio-rad FTS-7 FTIR along with a Harrick Model HTC-100 high temperature reaction cell was used for the *in situ* IR experiments. KBr windows were used due to their high IR transparency. Self-supported titania wafers were used for the IR experiments. Approximately 65–70 mg of powdered titania was compressed to form a 13-mm diameter and ~0.5-mm-thick self-supported wafer by using a Harrick Model PPE-S13 pellet piston die set and by applying a force of ~15,000 lbs with a Carver hydraulic press. The details of the IR experiments have been discussed elsewhere (4).

RESULTS

I. Initial Activity and Selectivity

The activity of the titania catalyst for CFC12 destruction under the two different reactant compositions is shown in Fig. 1 as a function of temperature. It can be noted that the activity was slightly greater when additional H_2O was present along with CFC12 and O_2. This effect of increased activity with additional water vapor was more pronounced with the CFC11 feed (4).

The selectivity of the titania catalyst at different temperatures and feed compositions is tabulated in Table 1. In the absence of water vapor in the feed stream, deep oxidation selectivity to CO_2 dropped drastically with temperature, falling from 100% at 400°C to 75.3% at 200°C. The partial oxidation products detected with the decrease in CO_2

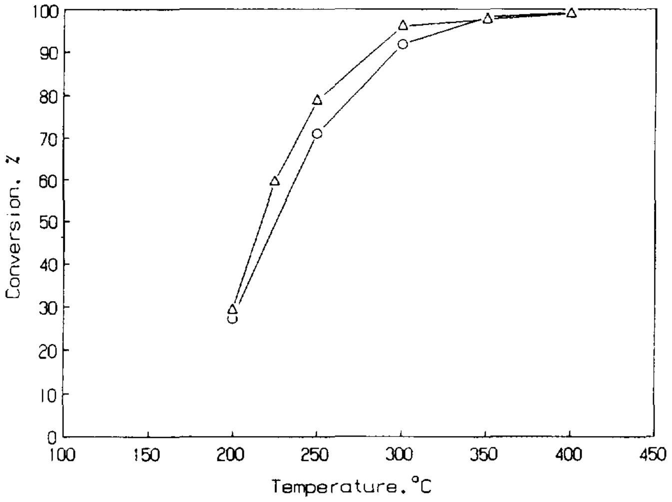

FIG. 1. Conversion of CFC12 on TiO_2 vs temperature. Space velocity = 10,500 h^{-1}. (○) CFC12/O_2, (△) CFC12/H_2O/O_2.

selectivity were (in the approximate order of decreasing magnitude) $COCl_2$, CFC11, and CFC13/CFC14[2]. The formation of titanium halides was evident from the solid yellowish white deposit at the colder section of the reactor exit, as discussed in more detail in the next section. A fraction of the halides formed was also trapped in the caustic bubbler connected at the reactor exit and was analyzed as halide ions in the solution. It should be pointed out that the amount of chloride detected in the trap solution was up to 5–6 times more than the amount of fluoride and hence, as listed in Table 1, chlorine balances for these experiments were much better (60–100%) than fluorine balances (12–76%). No product HCl was detected as there was not any source of hydrogen in the reactant stream.

In the presence of water vapor, selectivity to CO_2 improved significantly, remaining at 100% for all temperatures (400–200°C). With addition of water vapor the conversion of CFC12 was also 100% selective to HCl except for temperatures above 300°C, where a few ppm (<10) of chlorine was produced. However, even at higher temperatures, the chlorine balance was constituted primarily of HCl (≥97%). The chlorine balances for these experiments varied between 78 and 100% (Table 1).

The amount of F_2 and HF could not be estimated separately as fluorine was quantified by trapping F_2 and HF in a caustic bubbler, with further analysis of the trap solution using an ion selective electrode. Part of the HF produced also reacted with the silica in the glass reactor as was evident from the detection of SiF_4 in the GC/MS and also from the severe reactor wall etching. The fluorine balances were in the range of 39–89% (Table 1).

II. Stability of the Titania Catalyst

Deactivation experiments with the titania catalyst and CFC12 feed were first carried out at 5000 h^{-1} space velocity and at 300°C as the earlier deactivation experiments with the zeolite catalysts were carried out under these conditions (2–4). Results are shown in Fig. 2. Although rapid deactivation (initial 98% conversion dropped to ~43% within 48 h of operation) took place without water in the feed stream, no significant drop in activity could be noted at 5000 h^{-1} space velocity when water was present as a cofeed. In the absence of water in the feed, a semisolid yellowish deposit was formed at the reactor exit which solidified and turned white with time. XRD analysis of the white solid identified it as $TiOF_2$ as illustrated in Fig. 3. The peak at $2\theta = 37.5°$ was from the sample holder and did not correspond to $TiOF_2$. XRF analysis of the solid deposit also revealed the presence of Ti. Unfortunately fluorine cannot be detected in the XRF. A reduction in CO_2 selectivity was also noted during the deactivation experiment without water; however, the total drop was only ~3% (from 100 to 97%) after 48 h of operation. The decrease in CO_2 selectivity was accompanied by a corresponding increase in $COCl_2$ and CFC11.

At 5000 h^{-1} space velocity and in the presence of water in the feed stream, a steady CFC12 conversion of ~100% was obtained over a period of 4 days (Fig. 2). Since the conversion was so high (close to 100%) at 5000 h^{-1} space velocity, catalyst deactivation could remain obscured. Therefore, the deactivation experiment with water as a cofeed was repeated at a higher space velocity of 10,500 h^{-1}, which reduced conversion level to ~90%. The decrease in activity with time at 10,500 h^{-1} space velocity was also negligible (the initial conversion of 90% was reduced to 85% during the 4 days of the experiment) with CFC12, H_2O, and O_2 as the reactants. An initial increase in activity as evident from Fig. 2 during the first hour of operation was noted during this experiment and is discussed at length in a subsequent section. Deep oxidation selectivity to CO_2 and HCl remained at 100% for 4 days when water was present in the feed stream at both the space velocities of 5000 and 10,500 h^{-1}. Although, in the presence of water vapor in the feed stream the TiO_2 cata-

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[2] 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). Unfortunately these two compounds also had the same mass number of 69. Therefore, the small amounts of these compounds (0–2 ppm) produced during the experiments could not be quantified separately. Equal concentrations of CFC13 and CFC14 were present in the calibration gas standard used for calibrating the GC/MS and a single calibration curve was obtained for mass number 69. Based on this calibration, quantification of any CFC13 and/or CFC14 produced was performed assuming an equimolar mixture of both the gases and they have been referred to as CFC13/CFC14.

TABLE 1

Compilation of Results on the Titania Catalyst

Run	Temperature (°C)	Conversion (%)	Reaction Rate × 10^6 (g mole/h, m^2)	Selectivity to CO_2 (%)	Ratio HCl/Cl_2	C Balance (%)	Cl Balance (%)	F Balance (%)
Feed: 1500–2000 ppm CFC12 and 20% O_2								
340	400	99.1	3.7	100.0	0	90	89	13
341	350	98.2	5.4	99.8	0	90	59	12
342	300	91.9	3.3	99.0	0	97	100	23
343	250	71.1	2.7	95.3	0	93	104	38
345	200	27.2	1.5	75.3	0	93	101	76
Feed: 1500–2000 ppm CFC12, 5000–6000 ppm H_2O, and 20% O_2								
346	400	98.9	4.7	100.0	163.7	81	101	39
347	350	97.7	5.2	100.0	277.0	60	86	50
348	300	96.0	5.6	100.0	∞	64	78	44
349	250	78.7	4.1	100.0	∞	80	85	58
352	225	59.5	2.8	100.0	∞	98	103	82
350	200	29.2	1.7	100.0	∞	94	98	89

Note. Space velocity = 10,500 h^{-1}.

lyst did not bring about any significant decrease in CFC12 destruction activity or deep oxidation selectivity during the 4 days of operation, the loss in surface area was considerable (75%) as listed in Table 2 and also discussed below.

III. Effect of Fluorine on the Initial Activity of TiO_2 Catalyst

The first 90 min of the deactivation experiments shown in Fig. 2 that were carried out with CFC12 feed on the TiO_2 catalyst are replotted on an expanded scale in Fig. 4. An initial increase in catalyst activity, particularly during the experiment at 10,500 h^{-1} space velocity is apparent from Fig. 4. Fluorine in the reaction products, either in molecular or halogen acid form, was probably responsible for this initial increase in titania catalyst activity. Various experiments carried out with CFC12, water vapor, and oxygen as the reactants also supported this assumption as discussed next.

Figures 5A and 5B compare the effect of the CCl_4 feed (no fluorine in its molecule) and the CFC12 feed on the initial activity of the titania catalyst. As the conversion of CCl_4 was almost 100% at 300°C and 10,500 h^{-1} space velocity (Fig. 5A) (the conditions at which the initial activity trend was observed with the CFC12 feed), the experiment was repeated at a lower temperature (and hence conversion) with the CCl_4 feed (Fig. 5B). It is obvious from Fig. 5B that unlike CFC12 feed, CCl_4 feed did not increase the activity of the titania catalyst during the first hour of reaction.

TABLE 2

Effect of Exposure to Reaction Products and Temperature on Surface Area of the TiO_2 Catalyst

	Surface area (m^2/g) $\sigma = \pm 2$–5
Fresh TiO_2	170
$TiO_2/CFC12/H_2O/O_2$/4 days at 300°C	40
$TiO_2/CFC12/H_2O/O_2$/100 min at 300°C	80
$TiO_2/{\sim}12$ h at 300°C	170
TiO_2/7 h at 500°C	60

An experiment was carried out, as illustrated in Fig. 6, to investigate the nature of the fluorinated species (i.e., chemisorbed, chemically bonded, etc.) responsible for the initial increase in TiO_2 catalyst activity during CFC12 destruction. During this experiment, once CFC12 conversion on TiO_2 reached a steady state value at 250°C, the feed gases were disconnected and dry grade nitrogen was passed through the catalyst bed at a higher temperature (300°C) for ~2 h (region 1). Following the passage of nitrogen, feed gases were reconnected at 250°C and the conversion of CFC12 was found to be unchanged (73–77%). Passage of air at 300°C (region 2) through the catalyst bed for ~2 h also did not seem to affect the activity of the titania catalyst. However, following passage of water at 250°C (region 3), the activity of the titania catalyst decreased to its initial value (i.e., the activity at time $t = 0$) of ~54% which increased again to the steady state value of ~75% within 1 h of operation.

Finally, IR experiments were carried out to study changes in the surface acidity of the TiO_2 catalyst during the CFC12 destruction reactions using pyridine as the probe molecule. The pyridine/IR experiments were carried out *in situ* in the high temperature reaction cell at 300°C (same as the deactivation experiment temperature).

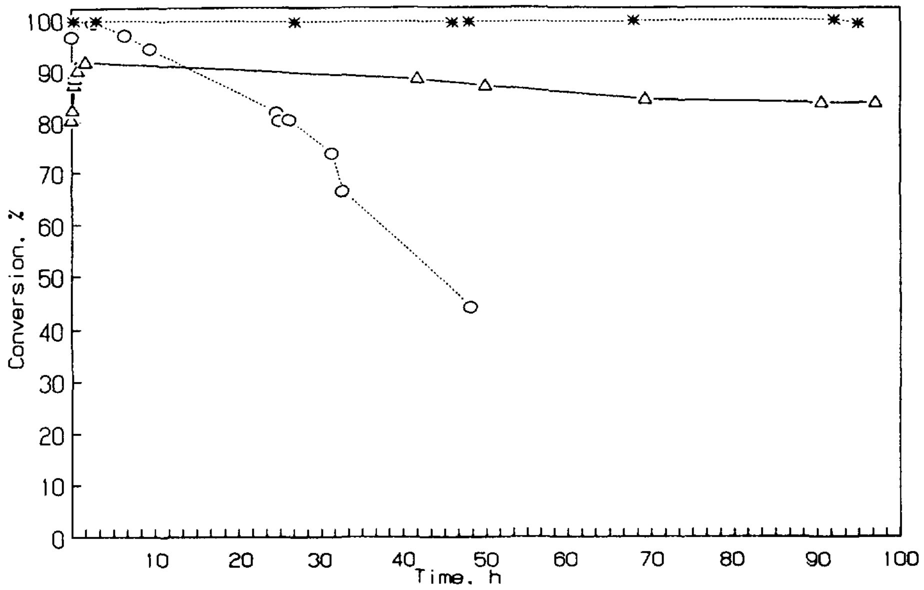


FIG. 2. Deactivation of TiO_2 for CFC12 feed at 300°C. (○) $CFC12/O_2$; (*) $CFC12/H_2O/O_2$, space velocity = 5000 h^{-1}; (△) $CFC12/H_2O/O_2$, space velocity = 10,500 h^{-1}.

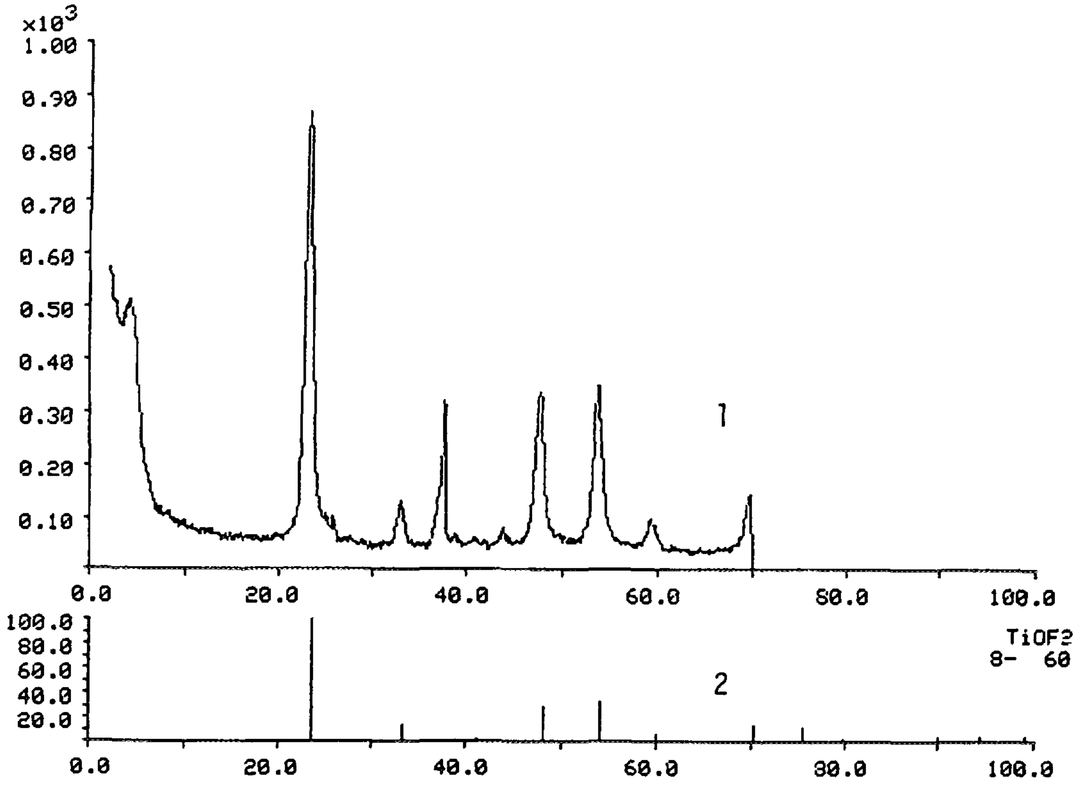


FIG. 3. X-ray diffraction spectrum of the solid reactor deposit. (1) Reactor deposit, (2) Reference $TiOF_2$ spectrum.

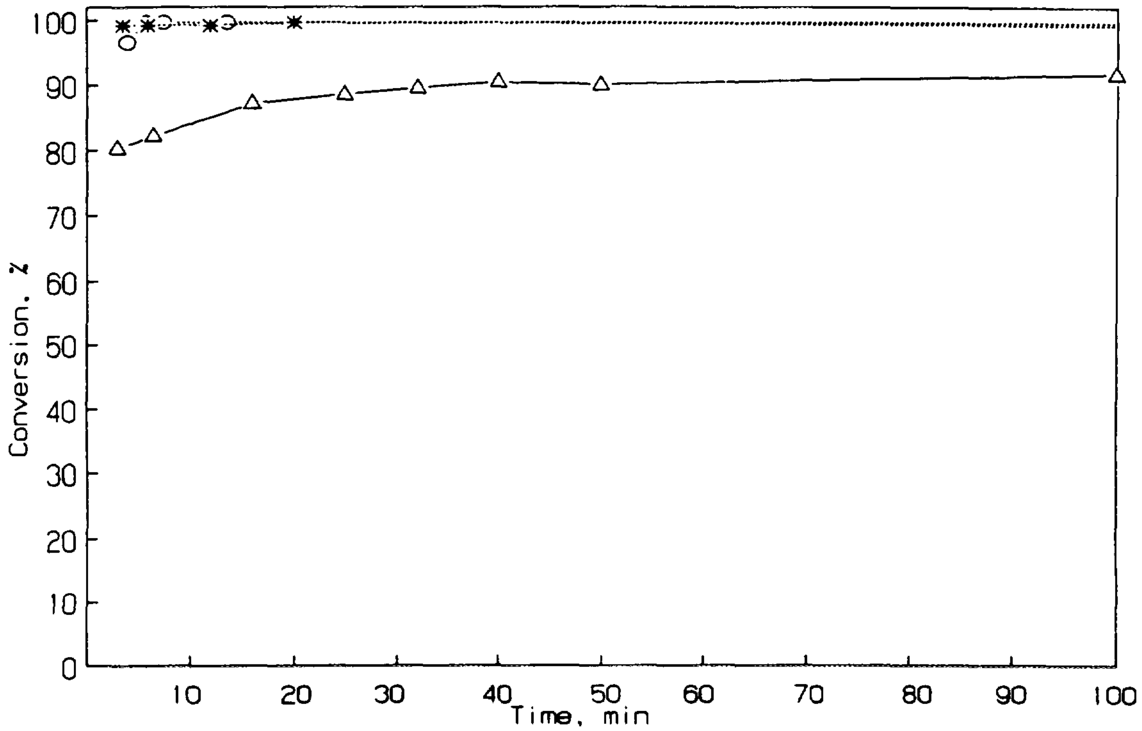


FIG. 4. Initial conversion of CFC12 on the TiO_2 catalyst at 300°C. (O) CFC12/O_2; (*) CFC12/H_2O/O_2, space velocity = 5000 h^{-1}; (△) CFC12/H_2O/O_2, space velocity = 10,500 h^{-1}.

Results of the pyridine/IR experiments are shown in Fig. 7. It can be noted that both Brønsted and Lewis acidity of the TiO_2 catalyst represented by the peaks at 1540 (due to pyridinium ion) and 1445 cm^{-1} (due to coordinately adsorbed pyridine), respectively, increased significantly as manifested by an increase in the intensities after ~90 min of CFC12 destruction reaction on the catalyst. The intensities of the absorbance spectra are also tabulated in Table 3. Since it was noted during an earlier experiment (Fig. 6) that passage of water through the activated catalyst bed reversibly brought the catalyst activity down to its initial activity, the effect of water on the activated catalyst was studied during the *in situ* IR experiment also. Passage of water over the CFC-treated TiO_2 catalyst gradually lowered both the Brønsted and Lewis acidities of the catalyst as noted from Fig. 7 and Table 3.

IV. *In Situ FTIR Studies*

In Situ FTIR studies were carried out to determine the reaction sites necessary for CFC12 adsorption on titania catalyst and also the reaction intermediates of CFC12 oxidation over this catalyst. A mechanism has been developed based on the results of the various reactor experiments reported above and also on the *in situ* IR experiments, results of which are reported next.

In the IR spectra of most oxides that have not been treated in any way, wide, intense adsorption bands are observed in the region above the lattice vibration region (>1200 cm^{-1}). This is due to adsorbed H_2O, CO_2, or other organic contaminants on the surface. Coordinative unsaturation of surface cations and anions leads to such adsorption. Heating at temperatures above 200°C with simultaneous evacuation usually removes most of the impurities from the oxide surfaces. Thus, the TiO_2 pellet was heated overnight in the IR cell at 300°C with simultaneous evacuation (100–200 millitorr) and the key features of the dry TiO_2 spectrum were found to be a band at 3640 cm^{-1} and an increase in absorbance below 1200 cm^{-1} and also above 3100 cm^{-1}. The band at 3640 cm^{-1} was from the O–H stretching vibration of the isolated OH groups or the Brønsted acid centers on the surface of the titania catalyst. The increase in absorbance below 1200 cm^{-1}, the so-called cutoff absorption frequency, was caused by absorption of IR by the bulk TiO_2. The poor transmission in the 3100–3900 cm^{-1} region was primarily due to absorption of IR by surface hydroxyl groups (14, 15).

The pure component gas phase absorbance spectrum of CFC12 had characteristic frequencies at 672, 930, 1103, and 1158 cm^{-1}, all of which are in the fundamental absorption region of bulk TiO_2 and would be obscured during *in situ* reactions due to the low transmission of IR in this region.

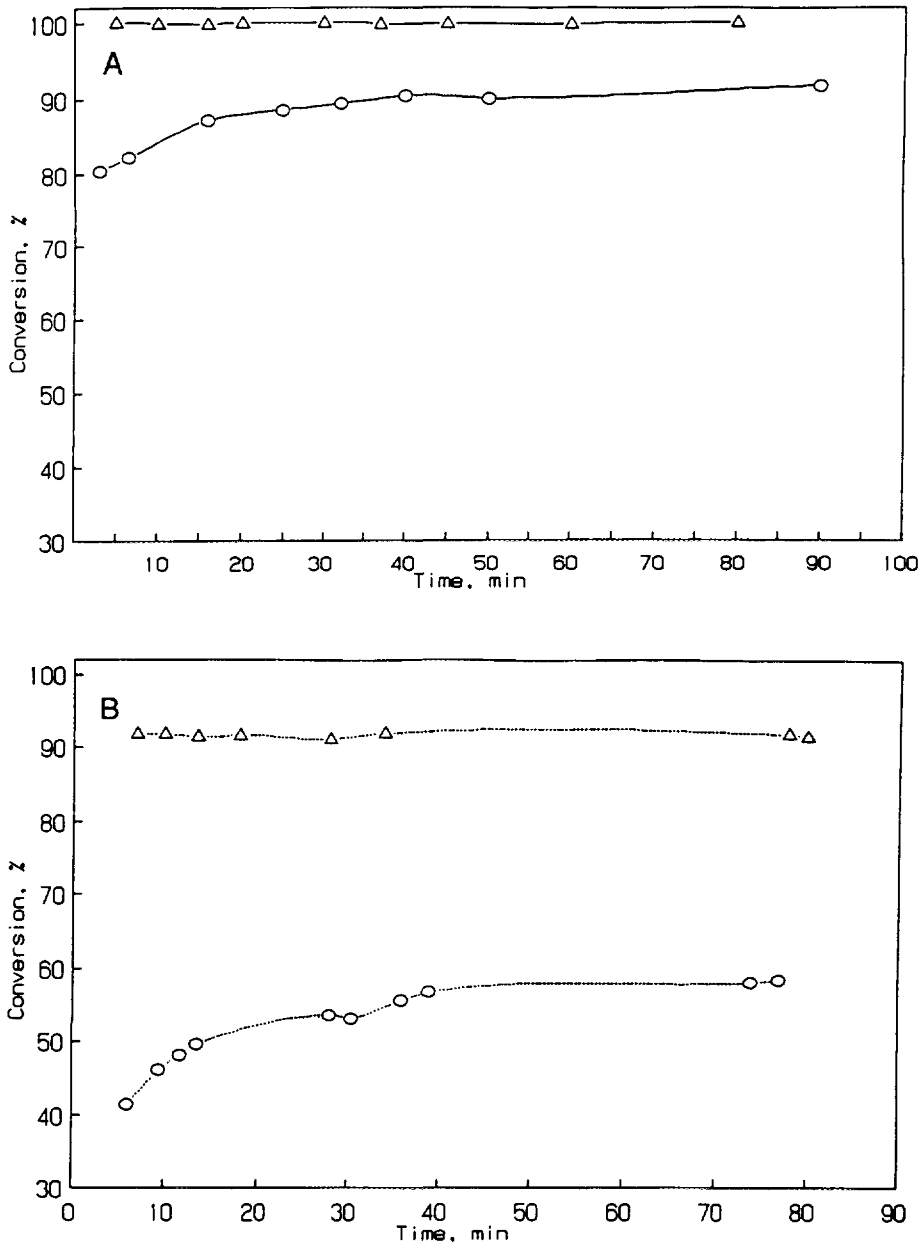


FIG. 5. Effect of fluorine content of the feed on the initial activity of the TiO_2 catalyst. (△) CCl_4 feed; (○) CFC12 (CCl_2F_2) feed. (A) Temperature = 300°C, space velocity = 10,500 h^{-1}; (B) Temperature = 250°C, space velocity = 21,000 h^{-1}.

After overnight evacuation at 300°C, oxygen was passed for ~3 h over the TiO_2 pellet at 300°C. Following the passage of oxygen, CFC12/N_2 mixture (~10,000 ppm CFC12) was passed for 1/2 h and continuous spectra were collected. The IR absorbance spectra of CFC12 reacting on TiO_2 at 300°C are shown in Fig. 8. The TiO_2 spectrum collected prior to reactions was used as the reference spectrum. A gradual and continuous development of a negative peak at 3640 cm^{-1} was noted during passage of CFC12 over the TiO_2 catalyst. Adsorption of the feed molecules on the surface hydroxyls (Brønsted acid sites) with simultaneous reaction between CFC12 and surface hydroxyls probably caused this decrease in intensity of the band at 3640 cm^{-1}. Experiments were also carried out (not illustrated here) by first adsorbing CFC12 (by passing CFC12/N_2 mixture) followed by the passage of oxygen. The decrease in intensity of the peak at 3640 cm^{-1} during the passage of CFC/N_2 was followed by a partial increase during the passage of oxygen indicating the freeing up of some of the surface hydroxyls. Similar results were also

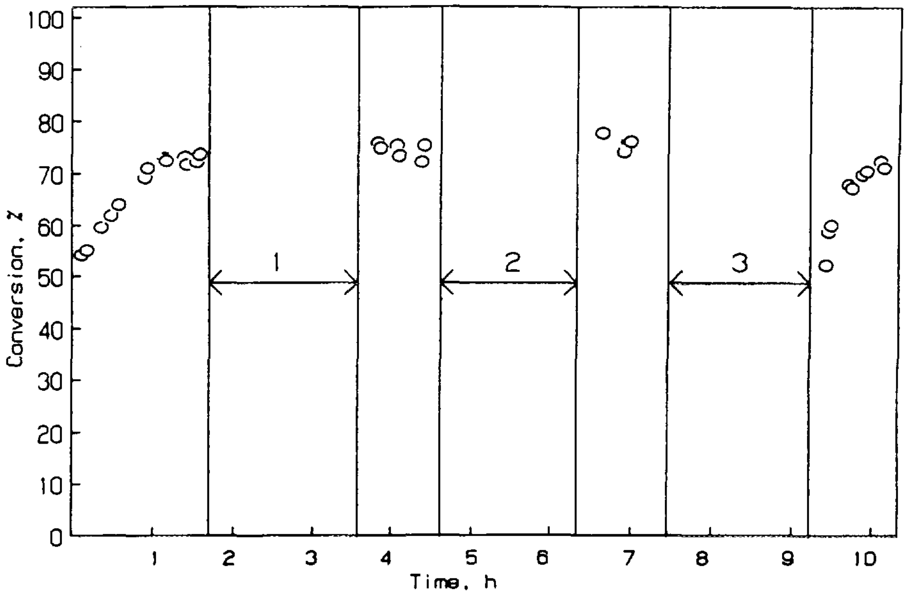


FIG. 6. Effect of water on increased activity of TiO_2; T = 250°C, space velocity = 10,500 h^{-1}. Region 1, N_2 at 300°C passing through the catalyst bed; region 2, air at 300°C passing through the catalyst bed; region 3, water at 250°C passing through the catalyst bed.

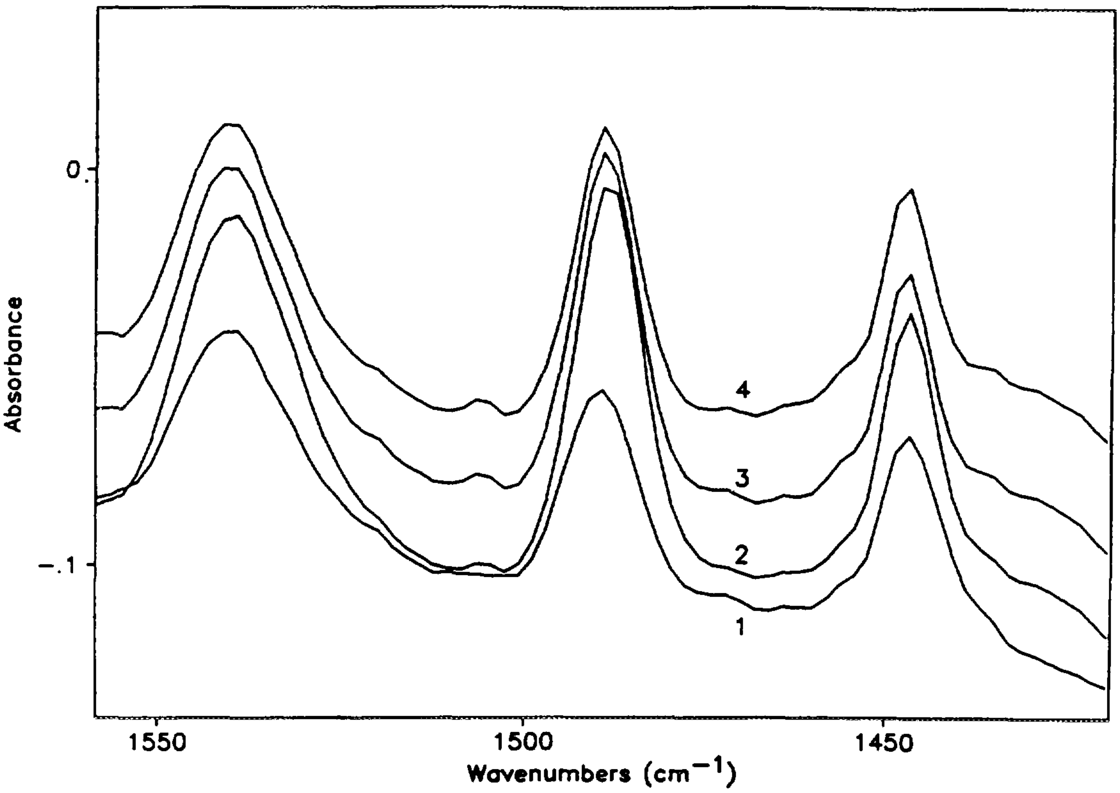


FIG. 7. IR absorbance spectra of chemisorbed pyridine on fresh and CFC12 treated TiO_2. (1) Fresh hydroxylated TiO_2, (2) CFC12-treated (for ~90 min) TiO_2, (3) H_2O passed for 1 h over CFC12-treated TiO_2, and (4) H_2O passed for 2 h over CFC12-treated TiO_2.

TABLE 3

Absorbance Intensities of Chemisorbed Pyridine on the Brønsted and Lewis Acid Sites of TiO_2 during CFC12 Reaction

	Brønsted ($1540\ cm^{-1}$)	Brønsted + Lewis ($1490\ cm^{-1}$)	Lewis ($1445\ cm^{-1}$)
Fresh dry TiO_2	0.35	0.33	0.50
Fresh hydroxylated TiO_2	0.45	0.31	0.28
CFC12 reacted for ~90 min	0.80	0.59	0.36
H_2O passed for 1 h after CFC12 treatment	0.65	0.47	0.30
H_2O passed for 2 h after CFC12 treatment	0.50	0.40	0.28

obtained with CCl_4 (4), a molecule very similar to CFC12. These results again supported the hypothesis that the drop in intensity of the band at $3640\ cm^{-1}$ (Fig. 8) was due to adsorption of CFC12 on hydroxyls and also destruction of surface hydroxyls due to reaction. The drop in intensity of the broad band centering at $\sim 3300\ cm^{-1}$ also indicated consumption of surface adsorbed water during CFC12 oxidation. Strong CO_2 peaks were also noticed at around 2320 and $2367\ cm^{-1}$ during the reaction. The peak at 1376 cm^{-1} was probably from a CO_2^- species adsorbed on the surface. Yates (16) assigned two strong peaks at 1580 and $1320\ cm^{-1}$ to the predominant CO_2^- species and peaks in the 2320–2360 cm^{-1} region to gas phase CO_2. Morterra *et al.* (17) also found a peak at $1320\ cm^{-1}$ apart from many others due to adsorption of CO_2 on anatase.

The most distinguishing feature was, however, the appearance of stretching frequencies in the 1800–1900 cm^{-1} region. Two peaks were observed at 1820 and $1886\ cm^{-1}$ during the CFC12 reaction. The presence of carbonyl stretches in this region is well established in the literature (18, 19). During CCl_4 oxidation on TiO_2, results of which have been reported elsewhere (4), a strong peak was observed only at $\sim 1820\ cm^{-1}$. This peak was attributed to $COCl_2$ as the C=O stretch of $COCl_2$ has been reported (19, 20) to appear in the 1800–1827 cm^{-1} region. Primet *et al.* (21) also observed upon adsorption of $COCl_2$ on TiO_2 bands similar to those shown in Fig. 8. Therefore, we assign the band at $1820\ cm^{-1}$ observed during CFC12 oxidation on titania to $COCl_2$ on the surface. The band at $1886\ cm^{-1}$ observed during CFC12 oxidation was probably from a COFCl species. As fluorine is more electronegative than chlorine, the inductive effect of fluorine reduced the length of the C=O bond and thus increased its force constant and the frequency of adsorption. Therefore, the C=O stretching frequency was shifted to a higher wave number ($1886\ cm^{-1}$). The C=O stretching

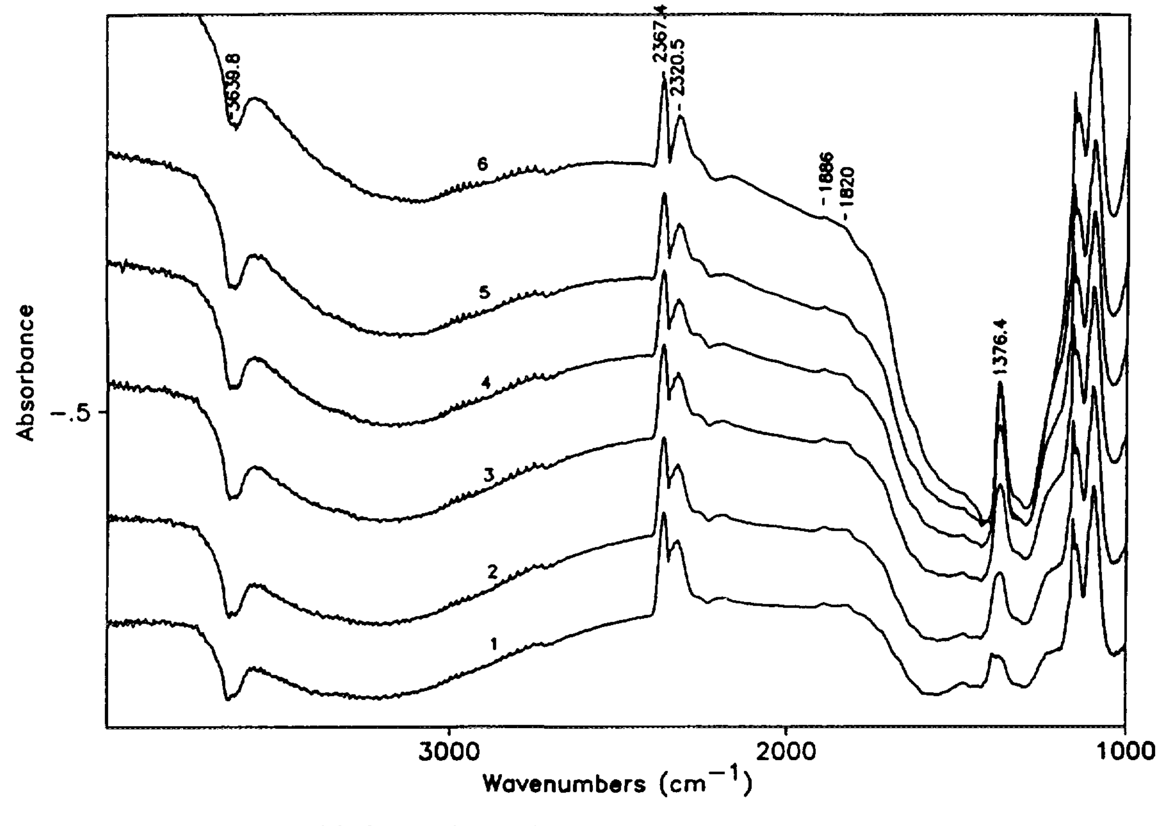


FIG. 8. IR absorbance spectra of CFC12 reacting on TiO_2 at 300°C. (1) 10 min, (2) 15 min, (3) 20 min, (6) 35 min of reaction.

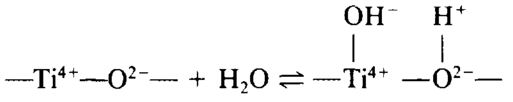
frequency of COFCl vapor has been reported to appear at 1868 cm^{-1} (19, 20). Chemisorption of COFCl on the surface of the TiO_2 catalyst probably caused the observed frequency shift to a higher wave number.

DISCUSSION

I. Initial Activity and Selectivity

It is apparent from the results presented in Fig. 1 and Table 1 that the presence of water vapor was necessary to obtain the maximum activity and CO_2 selectivity of the titania catalyst. The presence of water vapor was probably necessary to yield a higher Brønsted acidity of the catalyst. It will also be shown below, during the discussion of the reaction mechanism, that in the presence of both oxygen and water, water was the primary reactant in the oxidation of CFC12 to form CO_2, HCl, and HF. The origin of Lewis and Brønsted acidities in the TiO_2 catalyst and the role of water are well known (14, 15).

The surface coordinatively unsaturated cations in titania may accept free electron pairs of adsorbed molecules and therefore act as Lewis acid sites. In a hydroxylated environment, the dissociative adsorption of water on the coordinatively unsaturated cations and anions at the surface can also form Brønsted acid centers as shown below.



$$-\mathrm{Ti}^{4+}-\mathrm{O}^{2-}- + \mathrm{H_2O} \rightleftharpoons -\overset{\overset{\displaystyle \mathrm{OH}^-}{|}}{\mathrm{Ti}^{4+}}\ -\overset{\overset{\displaystyle \mathrm{H}^+}{|}}{\mathrm{O}^{2-}}-$$

Therefore, it is appropriate to relate the appearance of Brønsted acidity with hydroxylation and disappearance of Lewis acidity, and vice versa. IR pyridine experiments carried out in our laboratory also confirmed this. It is obvious from Table 3 that the hydroxylated TiO_2 had more Brønsted acid sites (higher intensity of the peak due to pyridinium ion at 1540 cm^{-1}) and fewer Lewis acid sites (lower intensity of the peak due to coordinately adsorbed pyridine at 1450 cm^{-1}) than did the dry (dehydroxylated) TiO_2.

Therefore, the presence of 5000–6000 ppm of water vapor in the reactant stream increased the activity of the TiO_2 catalyst by increasing the Brønsted acidity of the catalyst. It is well accepted in the literature (15) that oxidation of hydrocarbons on oxide catalysts is initiated by the adsorption of hydrocarbons on the Brønsted acid sites.

Detection of CFC11 and CFC13/CFC14 from the reaction between CFC12 and oxygen indicated the presence of dismutation reactions in the absence of water at lower temperatures. Dismutation of CFCs without water in the feed and at lower temperatures was noted with zeolite catalysts also (4). $COCl_2$ was also detected at lower temperatures. Further oxidation of $COCl_2$ to CO_2 at higher temperatures indicated a series mechanism where $COCl_2$ was formed as a reaction intermediate.

The titanium halides formed from the reaction between the catalyst and the product halogens either were deposited at the cold reactor exit or were hydrolyzed to titanium oxide and halogen acids in the caustic trap. The detection of more HCl than HF in the caustic trap was probably due to two reasons. First, titanium chlorides and oxychlorides are more volatile than titanium fluorides and oxyfluorides and therefore less of the chlorides were deposited on the reactor wall with more being transferred to the caustic bubbler. Second, fluorine, being more electronegative, could react with the chloride and oxychloride deposit on the reactor wall leading to the formation of chlorine which would easily be trapped in the caustic solution. The deposit on the reactor wall was indeed identified as $TiOF_2$, as discussed in the next section.

With the addition of 5000–6000 ppm of water into the reactant stream, deep oxidation selectivity of the titania catalyst was substantially improved. The probable reason was the easy hydroxylation of intermediate, such as $COCl_2$, forming CO_2 and HCl. Dismutation of CFC12 was also completely eliminated by the addition of 5000–6000 ppm of water indicating oxidative destruction to be the favorable reaction pathway in the presence of water. Addition of water also inhibited the formation of molecular halogens. The Deacon reaction did not take place appreciably except at temperatures above 300°C and even then a maximum of only 10 ppm of chlorine was detected at these temperatures.

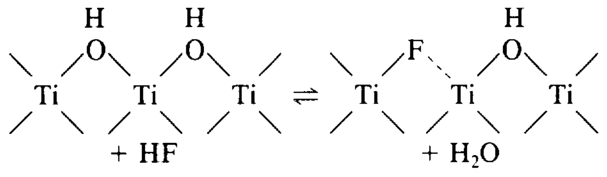
II. Stability of the Titania Catalyst

Deactivation of the TiO_2 catalyst was rather rapid without water in the feed stream (Fig. 2), primarily due to the loss of catalyst as halides and oxyhalides. The solid reactor deposit identified as $TiOF_2$ also supported this. The residual catalyst after 2 days of operation still had an anatase-type crystalline phase as revealed by XRD analysis. Although the activity of the catalyst deteriorated due to loss in catalyst weight and surface area, selectivity remained almost the same probably because there was no change in the crystalline phase.

Addition of water vapor into the feed stream facilitated the formation of less reactive HCl and HF as reaction products (as opposed to Cl_2 and F_2) (Table 1) and also swept away the acid products. Hence, it is probable that addition of water vapor lessened catalyst deactivation by eliminating the loss of catalyst as titanium halides and oxyhalides. The loss in surface area as shown in Table 2, however, indicated some interaction between the catalyst and the acid products. Surface fluorination, i.e., replacement of surface oxygen and/or hydroxyls by fluorine is the most probable reason for this loss in surface area.

Although the used catalysts did not have any detectable amount of chlorine or fluorine in them, surface fluorination was obvious from the increase in acidity during the first hour as discussed in the next section. XRD analyses of the used catalysts indicated primary existence of anatase-type titania with two new infinitesimal peaks (1–2% in intensity compared to the characteristic anatase peaks), which were attributed to the surface fluorine (or possibly chlorine) species.

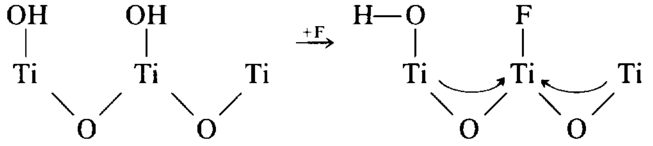
Loss in the surface area of titania catalysts at high temperatures is well established in the literature (22) and was also reconfirmed in our laboratory. Calcination at 500°C for 7 h caused a 65% drop in surface area of the TiO_2 catalyst. However, calcination at 300°C, the temperature at which the deactivation experiments were carried out, did not cause any reduction in surface area even after 12 h (Table 2). Therefore, temperature was not the reason for the decrease in surface area of the titania catalyst during CFC12 destruction in the presence of moisture. The loss in surface area was rather rapid during the first 1–2 h as noted in Table 2. The loss in surface area was almost 50% during the first 100 min of operation, whereas the total loss after 4 days was ~75%. In their review of fluorine-promoted catalysts, Ghosh and Kydd (23) also mentioned rapid initial decrease in the surface area of alumina catalyst upon fluorination, followed by a slower decrease. They also said that part of the alumina was consumed to form low surface area AlF_3 during fluorine promotion. We believe that in the presence of water vapor in the feed, a reversible reaction (as shown below) between surface oxygen/hydroxyl and fluorine exists which is responsible for the partial stabilization of the surface area after the first 1–2 h of operation. Due to the presence of this reversible reaction, fluorine retained in the catalyst was also negligibly small and could not be detected. More evidence supporting this is shown in the next section.



The loss in surface area was not accompanied by a drop in activity of the titania catalyst. Actually, activity increased during the first 1–2 h when the rate of reduction in surface area was greatest. The reason for this increase in activity was an increase in acidity as discussed in detail in the next section. Following the initial increase, the activity of the titania catalyst remained steady between 85 and 90% for 4 days, although the surface area experienced a gradual decrease from 80 to ~40 m^2/g. The opposing effects of slow decrease in surface area and slow increase in acidity was the most probable reason for the relatively stable activity of the titania catalyst. In their patent, Hashimoto *et al.* (12) have also recognized that, although their patented metal alloy catalyst (mixture of Ti, Zr, Nb, Ni, Co, etc.) was converted into fluorides during the decomposition of CFCs, it retained the high activity of decomposition. Further details, such as changes in surface area or acidity were, however, not mentioned.

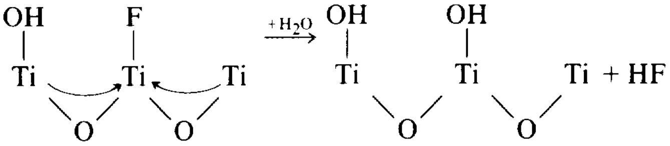
III. Effect of Fluorine on the Initial Activity of TiO_2 Catalyst

Partial replacement of surface oxygen and/or hydroxyls by more electronegative fluorine increased the polarity of the TiO_2 lattice, making the nearby Brønsted and Lewis acid sites more acidic, which was manifested by an increased activity for CFC12 destruction. Analogous experiments carried out with CFC12 and CCl_4 feeds (Fig. 5) indicated that only fluorine was capable of influencing the activity of the TiO_2 catalyst by polarizing the lattice. The increase in acidic strength through fluorine incorporation has also been reported by other researchers for various acidic catalysts such as zeolites [24, 25], mordenites [23], ZSM-type zeolites [26], and metal oxide catalysts (27–32). The fluorine substitution mechanism explaining the generation of stronger acid sites for the TiO_2 catalyst is shown below.



Two surface hydroxyls attached to two surface Ti^{4+}'s and a surface coordinatively unsaturated Ti^{4+} are shown on the left-hand side of the arrow. When fluorine replaces the hydroxyl attached to the Ti^{4+} in the middle, due to its higher electronegativity, fluorine pulls the electrons in the adjacent bonds towards itself. Consequently, the O–H bond is weakened, making the hydrogen more acidic, while the electron accepting capability of the coordinatively unsaturated Ti^{4+} is also increased, making it a stronger Lewis acid. The pyridine/IR experiments as shown in Fig. 7 and tabulated in Table 3 also confirm the acidity (both Brønsted and Lewis) increase of the TiO_2 catalyst after ~90 min of CFC12 destruction reaction.

It was suggested in the preceding section discussing the stability of the titania catalyst that in the presence of moisture in the feed the surface fluorination of titania was reversible due to hydration of the surface fluorine species; the experimental result as depicted in Fig. 6 also supports this. Passage of water over the TiO_2 catalyst with fluorine-increased activity reversibly brought the activity down to its initial value. Hydration of surface fluorine as shown below was believed to be responsible for the reversible nature of the increased activity of the titania catalyst.



Pyridine/IR experiments (Fig. 7 and Table 3) also demonstrated that the continuous passage of water over fluorinated TiO_2 slowly brought the acidity of the catalyst down to its original value. Retention of the increased activity after passage of N_2 and air at a higher temperature (300°C as compared to 250°C during reaction) indicated that the surface fluorine responsible for the activity increase was probably strongly adsorbed or chemically bonded to the surface.

IV. CFC12 Oxidation Mechanism

The probable CFC12 oxidation mechanism in the presence of water in the feed is discussed here, as the presence of water in the feed was necessary for the maximum activity, deep oxidation selectivity, and stability of the TiO_2 catalyst. In order to reduce noise and thus obtain a higher signal-to-noise ratio, water was not added during the *in situ* IR experiments. However, water present on the catalyst surface took part in the CFC12 oxidation reaction. The spectra of Fig. 8 were collected for only $\frac{1}{2}$ h and showed continuous decrease in intensity of the surface hydroxyls (3637 cm^{-1}) and surface adsorbed water (broad band at 3300 cm^{-1}), indicating the presence of both until the end of the experiment.

The *in situ* IR studies reported under Results showed that CFC12 feed was adsorbed on the surface hydroxyl sites of the titania catalyst. Experiments also identified $COCl_2$ and COFCl to be probable reaction intermediates. Detection of COFCl during CFC12 oxidation was possible only during the *in situ* IR studies. Although during the reactor runs reported earlier, small quantities of $COCl_2$ (<10 ppm) were detected by GC/MS from CFC12 under certain feed conditions, COFCl was never detected. Instability and also immediate hydrolysation were probably the reasons for COFCl being undetected during the reactor runs. *In situ* IR experiments carried out with CCl_4 feed and titania catalyst (results of which have been reported elsewhere (4)) also identified $COCl_2$ as a reaction intermediate during CCl_4 oxidation.

In order to establish the mechanism of CFC12 oxidation over titania catalyst it was also necessary to identify the roles of water and oxygen in this reaction. Results of the experiments carried out with 1500–2000 ppm of CFC12, 5000–6000 ppm of water vapor, and oxygen (~20%) in the feed stream were reported above under Initial Activity and Selectivity. To separate the effects of water and oxygen, experiments with the CFC12 feed were again performed with 5000–6000 ppm of water vapor, but without any oxygen in the feed. The results showed almost the same conversion of CFC12 without oxygen (<5% difference in conversion) as with oxygen. Deep oxidation selectivity of the catalyst was also only negligibly affected by the elimination of oxygen from the feed. Less than 10 ppm of $COCl_2$ was detected only at temperatures below 300°C. Therefore, elimination of oxygen from the feed by keeping the water concentration constant effected only insignificant change in activity and deep oxidation selectivity of the catalyst. This indicated primary participation of water in CFC12 oxidation over TiO_2 catalyst. It was also observed that only HCl was produced in the absence of oxygen in the feed, whereas reactor runs in the presence of oxygen (reported earlier) resulted in the production of Cl_2 along with HCl. This indicated that reaction between CFC12 and water generated HCl as the major product, and in the presence of oxygen the Deacon reaction was responsible for the production of some amount of Cl_2. This is also supported by another observation where experiments carried out with ~25,000 ppm of water and without oxygen in the feed (4) caused less of a drop in activity (~1% as compared to ~5% with both water and oxygen present) after 4 days of operation. As free halogens are more corrosive to catalyst, deactivation was reduced by completely eliminating oxygen from the feed and hence the Deacon-type reaction.

Based on all the above observations the following general reaction steps for the oxidation of a completely halogenated methane (CFC12, CCl_4, etc.) over TiO_2 catalyst in the presence of both water and oxygen are suggested.

1. $CX_4 + H^+ \rightarrow CX_4H^+$ (X = Cl or F)
2. $CX_4H^+ + OH^- \rightarrow COX_2 + 2HX$
3. $COX_2 + H_2O \rightarrow CO_2 + 2HX$
4. $4HX + O_2 \leftrightarrow 2H_2O + 2X_2$

Therefore, it is proposed that after becoming adsorbed on a Brønsted acid center (H^+), CFC12 reacts with neighboring surface hydroxyls (OH^-) to produce intermediates such as $COCl_2$ and COFCl, which further react with water to form complete oxidation products. The surface hydroxyls are probably replenished by dissociative adsorption of water on the catalyst. It should be mentioned that although the reaction steps suggested above (1–4) are speculative, they are reasonable based on the evidence presented here.

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