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The catalytic decomposition of CHF_3 over ZrO_2-SO_4

William B. Feaver, Joseph A. Rossin *

Guild Associates, Inc., 5750 Shier-Rings Road, Dublin, OH 43016, USA

Abstract

The destruction of CHF_3 over ZrO_2 and ZrO_2-SO_4 was studied in a fixed bed catalytic reactor system in dry and humid air streams. The addition of sulfate to the zirconia greatly improved the catalytic activity, decreasing the light-off temperature by approximately 40°C. The destruction of CHF_3 proceeded according to a catalyzed hydrolysis reaction, rather than an oxidation reaction, thereby necessitating that water be present in the feed stream. The presence of water in the feed stream had a significant effect on the stability of the catalyst. In dry air, the catalyst rapidly deactivated. Deactivation is attributed to the fluorination of the zirconium, which results in a loss of oxygen and sulfur from the catalyst and a significant decrease in surface area. The addition of 2.5% water to the feed stream greatly improves the catalyst's stability; however, some deactivation was observed. Deactivation in humid air was attributed to a gradual accumulation of fluorine on the catalyst, which resulted in a loss of sulfate and oxygen from the zirconia, and a decrease in the surface area of the catalyst.

Keywords: Catalyst; Fluoroform; Trifluoromethane; Oxidation; Zirconia

1. Introduction

Catalytic oxidation has been proposed as a means of destroying low (<1000 ppm) concentrations of halogen-containing organic compounds in air. For this technology to be viable, catalytic materials employed by the process must be both highly reactive and be able to function for extended periods of time in the highly corrosive acid gas environment. Supported platinum catalysts have been developed which are capable of destroying chlorine-containing organic molecules without significant loss of reactivity [1,2]. However, catalysts developed to oxidize fluorine-containing organic molecules have been less successful, due to deactivation brought about by catalyst support degradation [3–8]. In a study involving the oxidation of hexafluoropropene over a Pt/Al_2O_3 catalyst, Farris et al. [3] reported severe catalyst deactivation. Deactivation was attributed to a transformation of the high surface area alumina support to aluminum trifluoride. Imamura et al. [4] studied the oxidation of dichlorodifluoromethane over a titania-silica catalyst. The catalyst rapidly deactivated during the reaction exposure, with deactivation being attributed to loss of silica from the catalyst. Imamura et al. [5] later concluded that silica based oxidation catalysts would not be practical for the destruction of fluorine-containing organic molecules, due to catalyst support degradation resulting from loss of silica, likely as silicon tetrafluoride. The oxidation of hexafluoropropene was investigated over a TiO_2 catalyst using infrared techniques by Fan and Yates [6]. Although the catalyst was able to readily destroy hexafluoropropene, TiF_4 was detected in the gas phase. There is no doubt that the loss of titanium would cause the catalyst to deactivate. Loss of titanium has also been reported by Karmakar

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* Corresponding author.

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and Green [7] during the oxidation of dichlorodifluoromethane over a titania catalyst. In dry air, the titania catalyst rapidly deactivated, with deactivation being attributed to the formation and subsequent volatilization of $TiOF_2$. The addition of 5000 ppm water to the feed greatly improved the catalyst's stability, however, some deactivation was noted. Analysis of the catalyst following reaction exposure revealed a significant decrease in the catalyst's surface area, whether or not the run was conducted in humid air. Tajima et al. [8] investigated the decomposition of 1,1,2 trifluoro 1,2,2-trichloroethane over a W/TiO_2-ZrO_2 catalyst. The authors report the stable operation of the catalyst throughout the duration of a 140 h stability test. However, the authors report the presence of titanium and tungsten oxyfluorides in the lines down stream of the reactor. Bickle et al. [9] reported the stability of platinum on supported zirconia phosphate for the destruction of 1,1,2 trifluoro 1,2,2, trichloroethane. The resulting catalyst was much more stable than Pt supported on zirconia, and displayed no loss in reactivity throughout the duration of a 250 h run.

For catalytic technology to be successfully applied to the oxidation of fluorine-containing organic molecules, the catalyst must be able to maintain its integrity in the highly corrosive fluorine environment. In the present study, the stability of a sulfated zirconia (ZrO_2-SO_4) catalyst for the destruction of CHF_3 is investigated. CHF_3 is employed as a polymer blowing agent, and is also generated as a by-product during the manufacture of semiconductor material [10]. Compounds such as CHF_3 are coming under increased scrutiny due to their contribution to global warming. The atmospheric lifetime of CHF_3 is estimated to be 250 years [11]. The objective of the present study is to determine the mechanism by which CHF_3 is decomposed over a ZrO_2-SO_4 catalyst, and to evaluate the role of water in stabilizing the operation of the catalyst.

2. Experimental

2.1. Materials

Zirconium hydroxide was obtained from MEI Corporation. Chloroplatinic acid ($H_2PtCl_6 \cdot xH_2O$) was purchased from Aldrich. Trifluoromethane (98% purity) was purchased from DeLille Specialty Gases. A known quantity of neat CHF_3 was metered into a 16.7 L stainless steel pressure vessel. The vessel was then pressurized to 21 atmospheres using compressed air. The concentration of trifluoromethane in the pressure vessel was determined to be 5% (volume basis) using independent gas chromatographic techniques.

2.2. Catalyst preparation

ZrO_2-SO_4 was prepared by slurring 200 g of zirconium hydroxide in 500 ml of deionized water. The zirconium hydroxide was stirred overnight in order to break apart any clumps. In the morning, a 25 wt.% H_2SO_4 solution was prepared. The solution was added drop-wise to the zirconium hydroxide slurry until the pH of the slurry was 3.0. The pH of the slurry was maintained at 3.0 using the sulfuric acid solution. Following 8 h, the pH had stabilized and the slurry was placed in a high-density polyethylene pan. The slurry was dried overnight at 110°C in order to evaporate the water. The resulting solids were placed in a porcelain dish and calcined by heating from room temperature to 650°C at 5°C/min, with the final temperature maintained for 2 h. At the end of the 2 h, the resulting material was cooled to room temperature, then analyzed for surface area using a Nova 1200 BET analyzer. ZrO_2 was prepared by calcining zirconium hydroxide (used in preparation of the ZrO_2-SO_4) at 535°C for 2 h.

Product ZrO_2-SO_4 exists as a loose powder. In order to employ in the catalyst testing, the powder was pressed into wafers using a pellet press, then crushed and sieved to 40/60 mesh granules. The 1% Pt/ZrO_2-SO_4 catalyst was prepared according to standard wet impregnations techniques, using an aqueous solution of know platinum concentration. Following impregnation, the resulting material was dried for 2 h at 120°C, then calcined in flowing, humid air at 450°C for 12 h.

2.3. Equipment

Fig. 1 shows a schematic representation of the fixed bed catalytic reactor system. Compressed air from an oil-free compressor was purified using a PSA air drier. Purified air was metered to the system using a

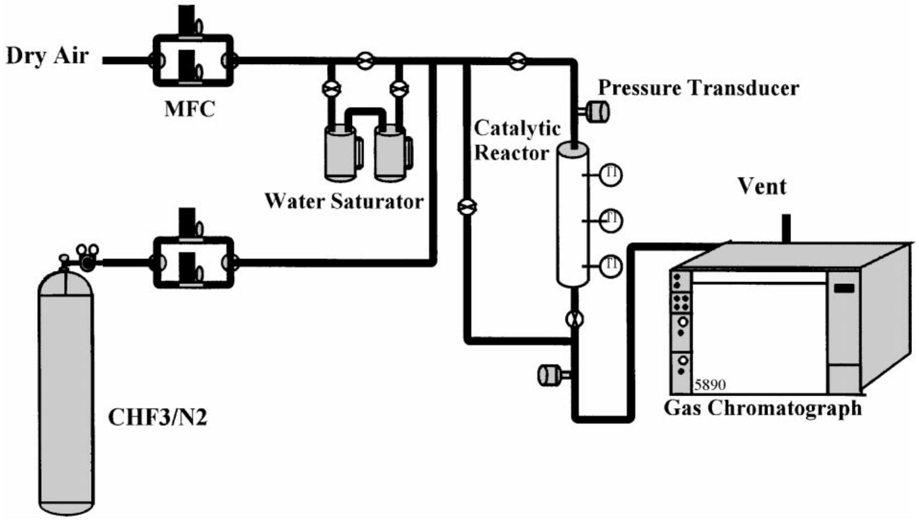

Fig. 1. Schematic representation of fixed bed catalytic reactor system.

0–500 Nml/min (Nml refers to 1 ml of air at 0°C, one atmosphere pressure) mass flow controller. Water was delivered to the system using a sparger system. The sparger system consists of a vessel filled with water located in a temperature controlled box. Incoming air is bubbled through the water in the vessel. A back pressure regulator, located downstream of the sparger is used to control the pressure of the air over the sparger vessel. The water concentration of the air stream is controlled by controlling the temperature and pressure of the sparger vessel. For runs conducted in the absence of moisture, the sparger system is by-passed using a pair of three-way ball valves.

CHF_3 from the stainless steel pressure vessel is metered to the system just upstream of a static mixer using either a 0–10 or 0–50 Nml/min mass flow controller. The feed stream then entered the catalytic reactor. The catalytic reactor consisted of a 0.95 cm o.d. 316 stainless steel tube approximately 25 cm in length. The reactor was surrounded by a 7 cm diameter by 20 cm long aluminum block which insured uniform heating of the catalyst bed. Reactor temperature was controlled by controlling the temperature of the aluminum block. This control scheme allowed for maintaining a stable catalyst bed temperature to within ±0.5°C of the setpoint value. Following the reactor, the effluent stream was sent to a Hewlett–Packard 5890 gas chromatograph for analysis. A blank run, performed with the reactor loaded with glass beads, was performed at the start of the testing. The reactor was inert; i.e., no conversion of CHF_3 was observed, at temperatures to 550°C.

The catalyst bed was suspended within the reactor on a plug of glass wool located approximately 8 cm from the bottom of the reactor. The catalyst bed was situated directly on the plug of glass wool. One type K thermocouple was extended from the top of the reactor to approximately one-third of the way into the catalyst bed. Although the axial temperature profile within the catalyst bed could not be monitored, deviation from isothermal operation could be assessed by comparing the catalyst bed temperature to that of the aluminum block surrounding the catalyst. Often, the catalyst bed is diluted with crushed glass of a similar mesh size in order to minimize axial temperature gradients. For these experiments, the catalyst bed was not diluted, so that following the run, the catalyst could be removed from the reactor and analyzed without diluent interfering with the analysis. Also, dilution with crushed glass would lead to the formation of SiF_4, which is a know catalyst poison. Failure to dilute the catalyst bed did not result in a significant axial temperature gradient (less than 3°C), based on a comparison between the temperature measured within the bed and the temperature of the aluminum block surrounding the reactor.

2.4. Reactor effluent analysis

The reactor effluent was analyzed on-line using a Hewlett–Packard 5890 GC equipped with an FID and TCD. CHF_3 was separated using a Porapak Q column and analyzed using the FID. The concentration of CO and CO_2 in the reactor effluent was determined using a 15 m-long by 0.32 cm-o.d. stainless steel column packed with carbosieve and analyzed using the TCD.

2.5. Catalyst characterization

N_2 BET surface area measurements were performed using a Quantachrome Nova 1200 BET surface area analyzer. When performing surface area analysis of the catalyst following reaction exposure, the entire catalyst bed was employed in the analysis. Following BET analysis, selected catalyst samples were analyzed using XPS spectroscopy. Care was taken to mix the sample so that the analysis would be representative of the entire catalyst bed. XPS analyses of catalyst samples prior to and following reaction exposure were performed using a Perkin–Elmer Phi 570 ESCA/SAM instrument. All binding energies were referenced to the C1s photoelectron peak at 285.0 eV.

3. Results and discussion

3.1. Reactivity screening and analysis

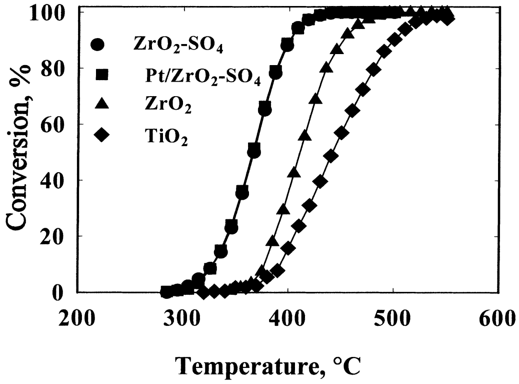

Fig. 2. Conversion of 3000 ppm CHF_3 in humid air as a function of reaction temperature for selected catalytic materials. $[H_2O] = 2.5\%$, $\tau = 0.4$ s.

Fig. 2 reports the conversion of 3000 ppm CHF_3 as a function of temperature in humid (2.5% water) air over ZrO_2, ZrO_2/SO_4 and 1% Pt/ZrO_2-SO_4. For comparison, results corresponding to TiO_2 (Degussa, P-25) are also reported. The residence time for all tests was 0.4 s. All tests were performed by heating the catalyst to either 500 or 550°C. Once at reaction temperature, the catalyst was exposed to 3000 ppm CHF_3 at the above stated process conditions. Following 1 h, the catalyst temperature was decreased at a rate of 40°C/h with the effluent stream being sampled for the concentration of CO, CO_2 and CHF_3 every 15 min (10°C temperature intervals). Results presented in Fig. 2 may be used to compare the relative reactivity of different catalytic materials. As Fig. 2 shows, both ZrO_2 and ZrO_2-SO_4 are much more reactive than TiO_2, which has demonstrated the ability to decompose fluorine-containing compounds in humid air [6,7]. Sulfating the zirconia significantly enhances the catalytic activity, decreasing the temperature required to achieve similar levels of conversion by approximately 40°C. The addition of sulfate to zirconia is known to increase the acidity of the resulting material [12]. This may at first suggest that the destruction of CHF_3 is an acid catalyzed reaction; however, the sulfate groups associated with zirconia are known to enhance the adsorption of water [13,14].

Interestingly, the addition of platinum to the catalyst had no effect on the catalytic activity. Platinum is known to be a highly reactive oxidation catalyst [15]. The fact that the addition of platinum did not affect the reactivity of the catalyst suggests that the destruction of CHF_3 is not proceeding according to an oxidative route. Metal oxides such as zirconia and titania are known to catalyze the destruction of halogen-containing compounds [1,6,7,9]. The addition of platinum to the catalyst did; however, alter the reaction product distribution. Reaction products for the destruction of CHF_3 over the ZrO_2/SO_4 catalyst consisted of mixtures of CO and CO_2, with the CO_2 selectivity being approximately 60% at the highest (500°C) reaction temperature, and decreasing with decreasing temperature. The addition of platinum to the catalyst (1% Pt/ZrO_2-SO_4) shifted the CO_2 selectivity to 100% at all conditions, eliminating the presence of CO in the effluent stream. Thus, although platinum does not contribute to the destruction of CHF_3, it does serve the role of oxidizing product CO to CO_2.

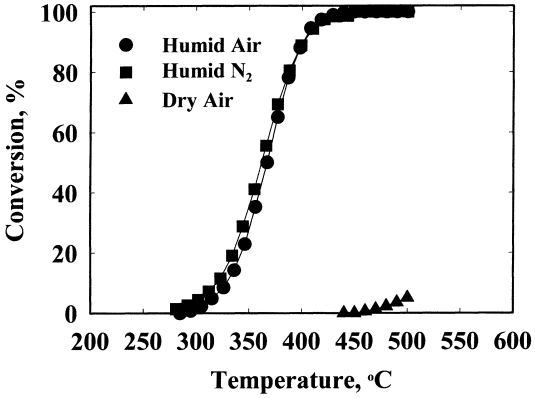

Fig. 3. Conversion of CHF_3 in dry air, humid N_2 and humid air as a function of reaction temperature over a 1% Pt/ZrO_2-SO_4 catalyst. $[CHF_3] = 3000$ ppm, $\tau = 0.4$ s.

Fig. 3 reports the conversion of 3000 ppm CHF_3 in humid air, humid N_2 and dry air as a function of reaction temperature over the 1% Pt/ZrO_2-SO_4 catalyst. All tests employed a residence time of 0.4 s. Tests performed with humid air and humid N_2 employed a water concentration of 2.5%. When performing the test in dry air, the catalyst was heated to 500°C in flowing dry air, and remained exposed to flowing dry air overnight prior to initializing the test. As the results show, the removal of oxygen from the feed stream does not, to within experimental error, affect the shape or position of the light-off curve. Water; however, has a significant affect on the catalytic activity. In the absence of water, the catalyst is essentially inactive. Results presented in Fig. 3 suggest that the destruction of CHF_3 is not proceeding according to an oxidative route, but rather via a catalyzed hydrolysis reaction.

Mixtures of CO and CO_2 were detected in the effluent stream when performing the test (Fig. 3) in humid N_2 over the 1% Pt/ZrO_2-SO_4 catalyst. The CO_2 selectivity decreased from about 75% at 500°C to less than 10% at 350°C. Only traces (less than 75 ppm) of CO_2 are present in the effluent stream when performing this test with the platinum-free ZrO_2-SO_4 catalyst. These results indicate that an additional role of platinum is to promote a reaction between water and CO to produce CO_2.

Two additional tests were performed in order to further verify the proposed catalyzed hydrolysis mechanism. Results of these tests are reported in Fig. 4. The first test involved recording the conversion of 3000 ppm CHF_3 as a function of time-on-stream in humid N_2. This test was performed at 400°C and a residence time of 0.4 s for the purpose of determining whether lattice oxygen is contributing to the reaction scheme, as per a Mars-van Krevelen mechanism [16]. Reaction products consisted of mixtures of CO and CO_2, with the CO_2 selectivity remaining nearly constant at 45% throughout the duration of the test (carbon balance was greater than 95%). The Mars-van Krevelen mechanism involves as the rate limiting step

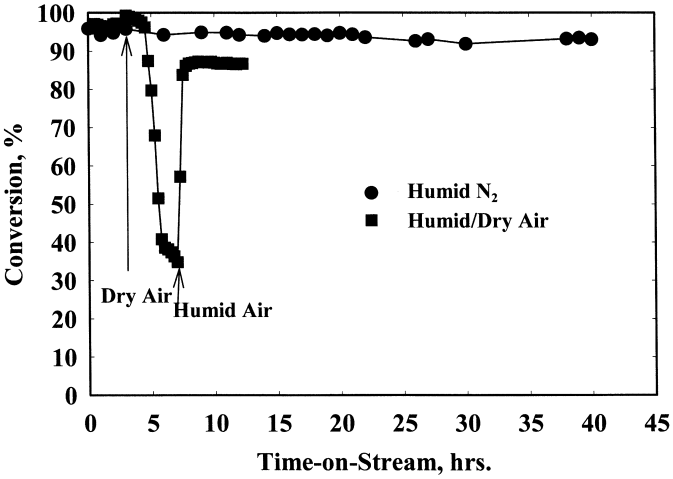

Fig. 4. Conversion of CHF_3 as a function of time-on-stream in humid N_2 and alternating humid and dry air over a 1% Pt/ZrO_2-SO_4 catalyst. $T = 400$°C, $[CHF_3] = 3000$ ppm, $\tau = 0.4$ s.

a reaction between gas phase reactant and lattice oxygen, with gas phase oxygen (O_2) regenerating the site. If the reaction is proceeding according to a Mars-van Krevelen mechanism, it would be difficult to detect changes in the catalyst activity from the light-off curve (Fig. 3), due to the short time frame over which the test is performed (about 3–4 h). If lattice oxygen were involved in the destruction of CHF_3, then one would expect the catalyst to deactivate over time, since there is no O_2 to replace the lattice oxygen being consumed during the reaction. Over the course of the 40 h test, approximately 0.05 mol of CHF_3 were consumed by approximately 0.012 mol of catalyst. This calculation clearly shows that there is not enough oxygen available in the system to account for the number of moles of CHF_3 converted to CO and CO_2. As results show, the catalyst remains relatively stable throughout the duration of the 40 h test, indicating that the reaction is not proceeding according to a Mars-van Krevelen type mechanism.

As a note, a mechanism involving CHF_3 and lattice oxygen, with water replenishing the oxygen lost from the lattice, was considered. A test was performed whereby the catalyst was exposed to dry air overnight at 400°C. In the morning, 3000 ppm CHF_3 in dry air was introduced to the feed. Virtually no conversion of CHF_3 (conversion less than 5%) was observed. If the destruction of CHF_3 was initiated over lattice oxygen, as per the above mechanism, an initial activity consistent with that reported in Fig. 4 would have been expected. Since no conversion was observed, it can be concluded that lattice oxygen is not directly responsible for the destruction of CHF_3.

Results of a second test presented in Fig. 4 dramatically illustrate the effects of water on the catalyst activity. The test was performed by exposing the catalyst to 3000 ppm CHF_3 in humid (2.5% H_2O) air at a residence time of 0.4 s at 400°C. Following 3 h on stream, the flow of water to the system was discontinued. After 7 h on stream, the flow of water was re-established. Approximately 1 h after discontinuing the flow of water, the conversion of CHF_3 begins to rapidly decrease. Upon re-establishing the flow of water, the conversion of CHF_3 rapidly increases, but to a level some-what below that recorded initially. The rapid deactivation upon removal of water from the feed stream is consistent with the proposed catalyzed hydrolysis mechanism. As the reaction proceeds, hydroxyl groups are consumed. The absence of water in the feed stream prevents the sites from being replenished, thus resulting in the observed deactivation. The re-introduction of water to the feed stream restores most, but not all, of the catalytic activity. This result indicates that the observed deactivation is reversible to some extent. Although a decrease in the conversion of CHF_3 from 97 to 88% upon re-introduction of water to the feed stream may not seem large at first glance, this decrease represents almost a 50% decrease in the first order rate constant. Evidently, removal of water from the process stream for even a short period of time has a significant effect on the activity of the catalyst.

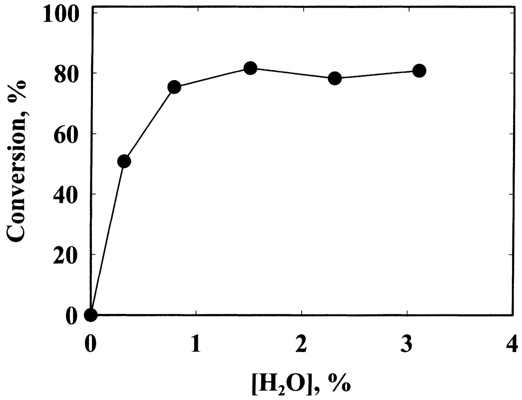

Fig. 5. Effects of water concentration on the conversion of CHF_3 over the 1% Pt/ZrO_2-SO_4 catalyst. $T = 385°C$, $[CHF_3] = 3000$ ppm, $\tau = 0.4$ s.

Fig. 5 reports the conversion of 3000 ppm CHF_3 as a function of the concentration of water in the feed stream. The test was performed at 385°C employing a residence time of 0.4 s in air. For tests performed with water concentrations below 1.5%, the catalyst was exposed to the process stream (less CHF_3) for a minimum of 12 h prior to initiating the test. Conversions reported represent the average of a 3–5 h reaction exposure. As results show, the reaction is zeroth-order with respect to water for water concentrations greater than about 0.8%. The zeroth-order dependency on the concentration of water is attributed to the surface of the catalyst being saturated with hydroxyl groups. Below this concentration, the surface is not saturated, and the reaction is positive order with respect to the concentration of water.

Based on results presented in Fig. 3 through 5, the overall reactions occurring on the surface of the catalyst proposed for the destruction of CHF_3 in humid air are:

$$H_2O + \equiv Zr–O–Zr \equiv \Leftrightarrow \equiv Zr–O–H\ H–O–Zr \equiv \qquad (1)$$

$$2 \equiv Zr–O–H + CHF_3 \Rightarrow \equiv Zr–O–Zr \equiv + CO + 3HF \qquad (2)$$

With the overall reaction (minus the oxidation of CO to CO_2 over platinum) being:

$$H_2O + CHF_3 \Rightarrow CO + 3HF \qquad (3)$$

Water interacts reversibly with the surface of the catalyst to form hydroxyl groups (Eq. (1)). The hydroxyl groups then react with CHF_3 to yield CO and HF, while regenerating the surface. In the destruction of CCl_2F_2 in the presence of water over a TiO_2 catalyst, Karmaker and Green [7] proposed a mechanism whereby CCl_2F_2 adsorbs on a Bronsted acid center and reacts with a neighboring surface hydroxyl to produce a COX_2 intermediate plus 2HX. It is possible that a similar reaction pathway may be occurring here; however, other mechanisms are possible. Other possible mechanisms include a reaction between surface hydroxyl groups and gas phase CHF_3 (Eley–Rideal mechanism), or a reaction involving the adsorption and subsequent decomposition of CHF_3 on the hydroxyl group. If the reaction involved adsorbed CHF_3 and gas phase H_2O, removal of water from the feed stream would have instantaneously decreased the reactivity (Fig. 4). Further, first order, rather than a zeroth-order dependency on the concentration of water would have been observed.

3.2. Catalyst stability

Fig. 6 illustrates the effects of water on the stability of the 1% Pt/ZrO_2-SO_4 catalyst during the destruction of 3000 ppm CHF_3. All results presented in this figure employed a residence time of 0.4 s at a reaction temperature of 400°C. All tests were performed by first heating the catalyst to 400°C in flowing, humid (2.5% water) air, with the process conditions maintained overnight. The pre-humidification of the catalyst was performed for the benefit of the test performed with dry air. If the test is initiated in dry air without pre-humidifying the catalyst, virtually no conversion of CHF_3 is obtained. In the morning, the concentration of water in the process stream was adjusted to its desired level (0.0, 0.3 or 2.5%). Once stable (about 1 h), CHF_3 was introduced to the feed stream, and the effluent stream was sampled for CHF_3 and CO_2. As results presented in Fig. 6 illustrate, the concentration of water in the feed stream has a significant effect on the stability of the catalyst. In the absence of water, the catalyst is rapidly deactivated. As discussed previously, the rapid deactivation of the catalyst is attributed to the consumption of residual surface hydroxyl groups. As the reaction proceeds, hydroxyl groups, present as a result of the pre-humidification of the catalyst, are consumed by the reaction. The conversion decreases as the reaction sites are consumed. Increasing the concentration of water to 0.3% slows, but does not prevent the catalyst from deactivating. Increasing the water concentration to 2.5% greatly minimizes, but does not eliminate deactivation.

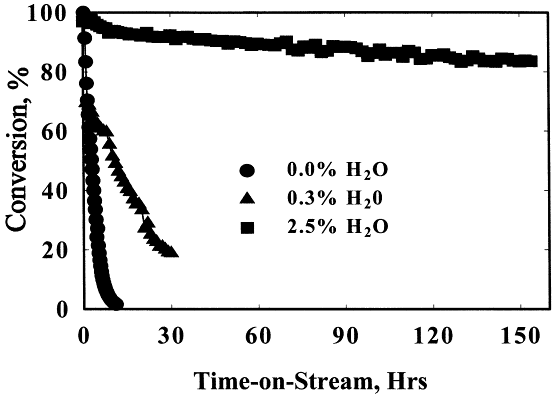

Fig. 6. Effects of water concentration on the stability of a 1% Pt/ZrO_2-SO_4 catalyst. $T = 400°C$, $[CHF_3] = 3000$ ppm, $\tau = 0.4$ s.

Fig. 7 reports the XPS spectra of zirconium 3d photoelectron region for the 1% Pt/ZrO_2-SO_4 catalyst prior to and following reaction exposure in dry (0.0% water) and humid (2.5% water) air. For the catalyst exposed to CHF_3 in humid air, both the shape and position of the zirconium 3d photoelectron peak are consistent with that of the unexposed sample, indicating that zirconium is able to maintain its integrity in the highly corrosive reaction environment. For the catalyst exposed to CHF_3 in dry air, significant changes to the zirconium 3d photoelectron peak are evident. The broadening of the peaks and loss of resolution

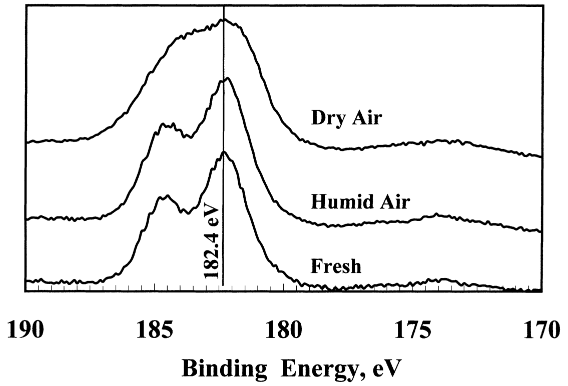

Fig. 7. XPS photoelectron spectra of the zirconium 3d photoelectron region for the 1% Pt/ZrO_2-SO_4 catalyst prior to and following reaction exposure in dry and humid (2.5% water) air.

Table 1
XPS and N_2 BET results for fresh and spent catalysts

	Fresh	10 h	30 h	37 h
		Dry air	0.3% H_2O	2.5% H_2O
XPS F/Zr	0	0.73	0.59	0.30
XPS O/Zr	2.06	0.75	0.97	1.38
XPS S/Zr	0.047	0	0	trace
(F/4 + O/2)/Zr	1.03	0.56	0.63	0.77
Surface area	95 m^2/g	17 m^2/g	21 m^2/g	67 m^2/g

between the $3d_{3/2}$ and $3d_{5/2}$ peaks is attributed to a partial fluorination of zirconium.

Table 1 reports the surface area and quantitative XPS analysis of the catalyst prior to and following exposure to CHF_3 for 10 h in dry air, 30 h in air with a water concentration of 0.3%, and following 37 h exposure to CHF_3 in air with a water concentration of 2.5%. The XPS atomic ratio (F/4 + O/2)/Zr in Table 1 represents a charge balance on the surface of the catalyst. As results presented in Table 1 show, significant changes in the surface area and elemental composition of the catalyst have occurred as a result of the reaction exposure. These changes are not attributed to thermal effects. Although not shown, no deactivation of the catalyst was evident following exposure to 300 ppm CHF_3 in humid (2.5% water) air for 120 h. Evaluation of the used catalyst revealed virtually no decrease in surface area and only a minimal amount of fluorine accumulation (XPS atomic F/Zr = 0.05). Virtually no change in the sulfate content of the catalyst was detected.

Characterization of the catalyst following exposure to CHF_3 in dry air reveals a significant decrease in surface area, and changes to composition of the catalyst: fluorine accumulation accompanied by a loss in surface oxygen, a loss of sulfate, and a charge deficient surface. As a note, the position of the F1s photoelectron peak (~686.0 eV) is consistent with that of metal fluorides [17]. No fluorine was observed at 690 eV, indicating the absence of polymerized fluorocarbons on the surface. Results presented in Table 1 suggest that fluorine is deposited onto the catalyst during the destruction of CHF_3, likely in the form of partially fluorinated zirconium. The interaction of fluorine with zirconia results in a loss of sulfate and oxygen from the catalyst, which is likely destabilizing the zirconia, leading to the observed decrease in surface area. The effect of increasing the water concentration in the feed stream is to minimize interactions between fluorine and zirconia, and thereby increasing the stability of the catalyst.

Even when employing a water concentration of 2.5%, catalyst deactivation is still evident. As a note, although platinum did not affect the activity of the catalyst, it is possible that platinum may have a role in stabilizing the activity of the catalyst over time. This is because platinum is known to dissociate water, whereby the dissociated water may play a role in removing fluorine from the surface of the catalyst. A platinum-free ZrO_2-SO_4 catalyst was exposed to CHF_3 for approximately 150 h under the conditions reported in Fig. 6. To within experimental error, the rate of deactivation was the same as that of the 1% Pt/ZrO_2-SO_4 catalyst. This result indicates that the addition of platinum to the catalyst does not enhance the catalyst's stability.

In an attempt to investigate the cause of the deactivation under humid conditions (2.5% water), the catalyst was evaluated for changes in its physical properties over the course of the reaction exposure. This was accomplished by exposing the catalyst to CHF_3 at the process conditions described in Fig. 6. Once the desired time was achieved, the run was terminated and the catalyst was removed from the reactor and analyzed using N_2 BET and XPS. Fig. 8 reports the surface area of the catalyst as a function of time-on-stream during exposure to 3000 ppm CHF_3

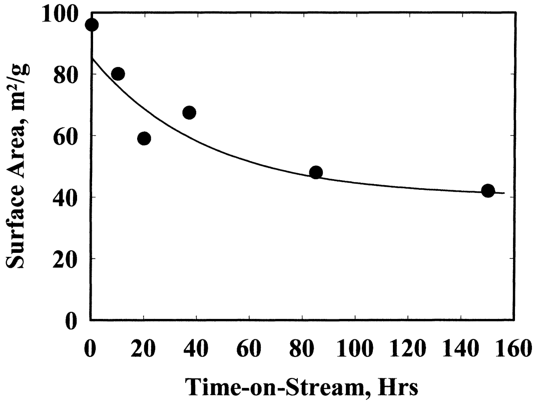

Fig. 8. Surface area of the 1% Pt/ZrO_2-SO_4 catalyst as a function of time-on-stream during exposure to CHF_3. $T=400°C$, $[CHF_3]=3000$ ppm, $[H_2O]=2.5\%$, $\tau=0.4$ s.

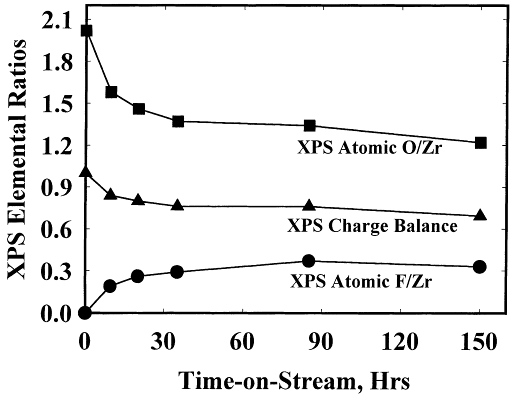

Fig. 9. XPS atomic rations as a function of time-on-stream for the 1% Pt/ZrO_2-SO_4 catalyst during exposure to CHF_3. $T=400°C$, $[CHF_3]=3000$ ppm, $[H_2O]=2.5\%$, $\tau=0.4$ s.

in humid (2.5% water) air. The surface area of the catalyst decreases faster during the first 20–40 h of reaction exposure. After this time, the rate of change in the surface area of the catalyst is much slower.

Fig. 9 reports XPS atomic O/Zr, F/Zr and charge balance as a function of time on stream during exposure to 3000 ppm CHF_3 in humid (2.5% water) air. These samples are identical to those whose results are reported in Fig. 8. Results illustrate that fluorine is rapidly accumulating onto the catalyst during the first 20 or so hours on stream. During this time, a rapid decrease in the oxygen content and the charge balance is observed. Although not shown, the sulfate content of the catalyst is decreasing early in the run such that at 37 h, only a trace of sulfate is detected. The decrease in the sulfate content coupled with the rapid increase in the fluorine content suggests that fluorine is displacing sulfate from the catalyst. At this point in time, we do not know the mechanism by which this is occurring. After the first 20 h of reaction exposure, the surface area, and oxygen content of the catalyst continue to decrease, and the fluorine content continues to increase, but at a much slower rate. These changes likely affect the concentration and strength of the surface hydroxyl groups, and lead to the observed deactivation.

Although not shown, (and difficult to quantify because of the low signal-to-noise), the vast majority of the sulfate associated with the catalyst is lost during the first 20 h of reaction exposure. At the end of the 150 h reaction exposure, no sulfur was detected on the catalyst using XPS.

One possible explanation for the rapid accumulation of fluorine on the catalyst during the first 20 h of reaction exposure may be due to an interaction between fluorine (as product HF formed during the decomposition of CHF_3 or elemental fluorine present on the surface of the catalyst) and defects on the zirconium. Alternatively, this behavior may be due to fluorine displacing sulfate, and is consistent with the observed rapid decrease in the sulfate content of the catalyst during the first 20 h of reaction exposure.

As shown in Fig. 2, sulfating the zirconia greatly enhances its reactivity. The reactivity enhancement is attributed to the sulfate increasing the concentration of hydroxyls on the catalyst [13,14]. With the loss of sulfate, one would expect the activity of the catalyst (2.5% water) to decrease at a much faster rate than that reported in Fig. 6. One possible explanation is that the replacement of sulfate with the highly electronegative fluorine does not strongly affect either the concentration or reactivity of the surface hydroxyl groups.

Results presented in Fig. 6 through 8 and in Table 1 allow us to speculate as to the role of water in stabilizing the activity of the catalyst. Expanding on the mechanism proposed previously, CHF_3 is decomposed over surface hydroxyl groups to yield HF, CO and surface fluoride:

$$\equiv \text{Zr–OH} + \text{CHF}_3 \Rightarrow \equiv \text{Zr–F} + 2\text{HF} + \text{CO} \qquad (4)$$

Gas phase water then interacts with the surface fluoride to yield HF while regenerating the surface, with the reaction being reversible:

$$2 \equiv \text{Zr–F} + \text{H}_2\text{O} \Leftrightarrow \equiv \text{Zr–O} - \text{Zr} \equiv + 2\text{HF} \qquad (5)$$

Alternatively, the surface fluoride may interact with adjacent hydroxyls to yield HF while regenerating the surface, with the reaction being reversible:

$$\equiv \text{Zr–F} + \equiv \text{Zr–OH} \Leftrightarrow \equiv \text{Zr–O–Zr} \equiv + \text{HF} \qquad (6)$$

From the above reaction scheme (Eqs. (4–6)), there is no mechanism for the removal of surface fluorine in the absence of water. Consequently, the removal of water from the feed stream results in irreversible damage to the catalyst.

In the case where the concentration of water is less than that required to saturate the surface of the catalyst (0.3%), rapid deactivation of the catalyst occurs because the rate of fluorine removal is not sufficient to prevent fluorine from destabilizing the zirconia.

4. Conclusions

1. The destruction of CHF_3 over Pt/ZrO_2-SO_4 proceeds according to a catalyzed hydrolysis reaction involving the sulfated zirconia. The role of platinum is to convert product CO to CO_2.
2. Sulfating the zirconia enhances the catalytic activity by increasing the concentration of surface hydroxyls.
3. Water is necessary to minimize deactivation of the catalyst. The role of water in stabilizing the catalyst is to provide a mechanism for the removal of surface fluorine.

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