JOURNAL OF CATALYSIS **168,** 482–490 (1997)
ARTICLE NO. CA971660

Catalytic Hydrolysis of Dichlorodifluoromethane (CFC-12) on Sol-Gel-Derived Titania Unmodified and Modified with H_2SO_4

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Received October 28, 1996; revised February 6, 1997; accepted February 17, 1997

Catalytic hydrolysis of dichlorodifluoromethane (CFC-12) in a humid air stream was studied over pure and sulfate promoted TiO_2 catalysts which were prepared by sol-gel methods. The results showed that complete conversion of CFC-12 on unmodified TiO_2 was achieved at reaction temperatures higher than 340°C under the employed reaction conditions. The selectivity to CO_2 ($[CO_2]_{produced}/[CFC\text{-}12]_{converted}$) varied from 0.5 to 0.88 over the range of 250–350°C and $CClF_3$ (CFC-13) was detected as the main by-product. Surface fluorination of the TiO_2 catalyst during the reaction improved its activity, induced the formation of the fluorinated by-product CFC-13, and changed such properties of the catalyst as its specific surface area, pore size distribution, and crystal size. It was found that the catalytic and structural properties of TiO_2 were greatly improved by sulfation. The sulfated TiO_2 (TiO_2/SO_4^{2-}) exhibited excellent reaction activity and selectivity for CFC-12 catalytic decomposition at low reaction temperatures (190–250°C) while retaining a stable structure. Complete decomposition of CFC-12 with stoichiometric production of CO_2 was observed over the TiO_2/SO_4^{2-} catalyst at 250°C under otherwise identical reaction conditions as used for pure TiO_2. Results of catalyst characterization by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and N_2 sorption analysis indicated that surface sulfate species formed on the sulfated TiO_2. When compared to unmodified TiO_2, the sulfated TiO_2 exhibited higher resistance to crystal phase transformation from anatase to rutile, higher resistance to the deleterious effects of fluorination of the catalyst, and higher specific surface area. Fluorination of the catalyst did not improve the activity of sulfated TiO_2 and no CFC-13 was detected as a by-product, indicating that fluorine was not involved in the formation of reaction sites over the sulfated TiO_2 catalysts. ⓒ **1997 Academic Press**

INTRODUCTION

Considerable evidence indicates that chlorofluorocarbons (CFCs) are a major cause of ozone depletion. Although the "Montreal Protocol on Substances That Deplete the Ozone Layer" bans the production of CFCs in industrialized countries, ozone depletion will continue as CFCs presently in the troposphere move into the stratosphere and are replaced by CFCs that leak out of existing equipment. Therefore, there is significant concern over the release of CFCs to the environment from these devices. This concern emphasizes the need for technologies that can destroy CFCs either prior to or during their release to the environment.

CFCs can be destroyed using techniques such as chemical reaction with sodium oxalate (1), reduction with sodium naphthalenide (2) or hydrogen (3), decomposition by solar energy (4), decomposition on activated charcoal (5), and incineration (6). However, catalytic decomposition appears to be the most practical and energetically favorable approach, especially for treating small and/or dilute sources of CFCs. Some research has been done, mostly in the past 5 to 6 years, to explore the applicability of catalysts for the destruction of CFCs (7–14). Catalysts that have been tested cover a wide range of metals (e.g., Pt, Au, Ni, and Pd), single and mixed metal oxides (e.g., TiO_2, Co_3O_4, Fe_2O_3, Mn_2O_3, SiO_2/Al_2O_3, TiO_2/SiO_2, CuO/TiO_2, and ZrO_2/MoO_3), zeolites and molecular sieves (e.g., H−Y, Co−Y, Cr−Y, and 13X), metal oxides supported on activated carbon (e.g., Fe_2O_3/C, Cr_2O_3/C, and CuO/C), and amorphous alloys (e.g., various alloys of Ti, Zr, Nb, Co, Ru, Rh, Pd, Ir, and Pt). The typical reaction temperatures employed in these catalytic decomposition studies were 300–500°C.

Recently, new types of nonzeolitic solid superacids, namely single or binary metal oxides (ZrO_2, TiO_2, Fe_2O_3, TiO_2–SiO_2, NiO−ZrO_2 etc.) modified by sulfate ions, have been developed (15–21). These materials exhibit extremely high activities for various acid-catalyzed reactions such as skeletal isomerization of butane, ring-opening isomerization of cyclopropane, alkylation of benzene derivatives, cracking of paraffins, and dimerization of ethylene (22–28). However, there are only a few citations in the patent literature for using solid superacids as catalysts for the decomposition of CFCs (14). Furthermore, we could not find a detailed characterization and mechanistic study of this reaction in the contemporary literature. In the patent literature (14), it has been reported that, with a contact time of 2 s and at an input temperature of 400°C, many organic halogen compounds such as CF_2Cl_2 (CFC-12), $CFCl_3$, CCl_4, CF_2ClBr, and CF_3Br in the gaseous phase can be hydrolyzed

0021-9517/97 $25.00

quantitatively into CO_2 and hydrogen halides using sulfated TiO_2 catalysts. Also, under the same conditions a temperature of 450°C was required for the complete hydrolysis of CF_3Cl (CFC-13).

In the present work, a sulfated TiO_2 solid superacid catalyst (TiO_2/SO_4^{2-}) having high specific surface area and high structural stability, prepared by a sol-gel method, was found to be quite active for the hydrolysis of CFCs. Complete decomposition of CFC-12 (employed as a model compound) into CO_2 was obtained at temperatures as low as 250°C on the sulfated catalyst. This study involves a preliminary investigation into the mechanism of the decomposition of CFC-12 over this catalyst. The influence of sulfation on the catalytic and physicochemical properties of the TiO_2 substrate was investigated in detail using XRD, XPS, FTIR, and N_2 sorption. For comparison, the properties of the corresponding unmodified TiO_2 catalyst are also reported.

METHODS

Catalyst Synthesis

Titanium dioxide aggregates were prepared using a sol-gel technique that involved the controlled hydrolysis of titanium tetraisopropoxide followed by dialysis to pH ∼ 4 (29). Particle aggregates having diameters between 0.25 and 0.5 mm were then obtained by evaporation of the solvent, firing to the desired temperature, grinding, and sieving. Full details of this preparation method were presented in an earlier paper (30).

Sulfated catalysts with SO_4^{2-} content of 9 wt% were obtained by impregnating the dried TiO_2 xerogel (0.25–0.5 mm in diameter prepared as previously described) with 1 *M* H_2SO_4 solution (1 ml/g TiO_2). This sample was then dried in air at 110°C for 3 h, and finally calcined in air for 3 h at desired temperatures, typically 500°C. We employed 0.50 g of the catalyst in all of our reaction studies.

Characterization of Catalytic Activity

Studies of the catalytic hydrolysis of CFC-12 were conducted at atmospheric pressure by using a fixed-bed tubular reactor operated in a noncirculating mode and interfaced with a Hewlett–Packard GCD System (HP G1800A GCD). The tubular reactor (12 cm long and 6 mm inner diameter) was constructed of Pyrex with a long inlet preheating section packed with pellets of inert α-alumina (Aldrich, 99.8% purity, $\leq$3 mm). Reaction temperature was varied by using an electric furnace and a temperature controller (Glas Col D.T.II). CFC-12 was obtained in a compressed gas cylinder at a concentration of 1001 ppmv ±2%, with the balance of gas being zero air containing <0.1 ppm total hydrocarbons (Scott Specialty Gases). The gas stream was humidified by passage through a water saturator, and the water content in the reactant stream was fixed by controlling the flow rate and the temperature of the saturator. The humidified feed (996 ppm CFC-12 and 5400 ppm H_2O in air) passed through the catalyst bed at a flow rate of 50 ml/min.

All measurements reported in this paper were obtained at steady state conditions (with the exception of data shown in Fig. 8), typically after operating the reactor for 5 h. In general, steady-state conditions were reached after about 0.5 and 3 h of operation with the TiO_2/SO_4^{2-} and TiO_2 catalysts, respectively.

Reactor inlet and effluent gas mixtures were analyzed using a Hewlett–Packard GCD System. This unit combines a gas chromatograph, an electron ionization detector, and a data analysis system to generate not only traditional retention time and abundance information but also mass spectral data for each sample component. The GCD System employed a Carboxen 1006 Plot capillary column (30 m length, 0.32 mm i.d.) with the column temperature held at 35°C for 3 min, raised to 185°C at 24°C/min, and held at 185°C for 6 min. The sampling loop volume injected into the GCD was 250 μl using He as the carrier gas at a column flow rate of 1.0 ml/min with an inlet temperature of 200°C and a detector temperature of 250°C.

Known concentrations of CFC-12 and carbon dioxide were utilized to calibrate the GCD System. Mass balances were not attempted for Cl and F because of the high reactivity of the halogenated products (7). One-hundred percent recovery of carbon was obtained under complete hydrolysis conditions when using the TiO_2/SO_4^{2-} catalyst. $CClF_3$ was detected as a by-product when using the pure TiO_2 catalyst. However, the concentrations of this by-product could not be quantified because we did not have a suitable standard. In addition, trace levels of carbon monoxide were detected when using both catalysts under conditions of incomplete hydrolysis. These peaks were too small to be integrated and quantified. No other by-products were detected.

Although our primary purpose in performing this study was not to obtain a detailed kinetic analysis of these systems, we did employ a theoretical analysis to estimate the influence of mass transfer processes on our observed reaction rates (31). These calculations indicate that, under all the reaction conditions employed in this study, external mass transfer did not control the reaction rate. In addition, the apparent activation energies for this reaction on both catalysts were ca. 45 kcal/mol. For systems in which the reaction rate is controlled by external mass transfer processes, activation energies are typically less than 5 kcal/mol. However, intraparticle mass transfer effects may have affected some of the observed reaction rates. While these effects did not appear to be significant for reactions over the pure TiO_2 catalyst, such effects may have influenced the reaction rates obtained over the TiO_2/SO_4^{2-} catalyst, especially when the conversion of CFC-12 was greater than ca. 50%. If more detailed kinetic studies are performed on these systems in the future, the experimental conditions will need to be modified to assure that the observed reaction kinetics are controlled by the surface chemistry.

Characterization of the Physicochemical Properties of the Catalyst

Specific surface areas of the fresh and used catalysts were determined by applying the BET method to the sorption of nitrogen at −196°C. X-ray diffraction analysis was performed using a Scintag diffractometer with Cu$K\alpha$ radiation. The crystallite size of anatase and rutile was calculated from peak halfwidths by using the Scherrer equation with corrections for instrumental line broadening. Percent composition calculations were made using

$$\%\ \text{rutile} = [1/([0.884A/R] + 1)] \times 100\%, \qquad [1]$$

where A is the area of the anatase peak, R is the area of the rutile peak, and the number 0.884 is a scattering coefficient. X-ray photoelectron spectroscopic analysis was carried out with a Perkin–Elmer PHI 5400 ESCA system using a Mg anode (15 kV, 20 mA). Binding energies were referenced to the C_{1s} level at 284.6 eV. Diffuse-reflectance FTIR spectra were recorded using a Nicolet Magna-IR 750 spectrometer and 20 mg of catalyst mixed with 200 mg of KBr.

RESULTS AND DISCUSSION

Effect of Sulfation on the Physicochemical Properties of the Catalyst

Crystal structure. The crystal structures of fresh or used TiO_2 and TiO_2/SO_4^{2-} catalysts calcined in air at different temperatures for 3 h were examined by X-ray diffraction (Fig. 1). For unmodified TiO_2, the primary crystal phase was anatase (90% anatase, 10% rutile) with an average crystallite size of 71 Å when the sample was calcined at 300°C. These TiO_2 samples underwent a dramatic phase transformation from anatase to rutile at temperatures higher than 400°C. After calcination at 500°C, the rutile form became the dominant phase in the sample (73% rutile) with an average crystallite size of 350 Å. In the case of TiO_2/SO_4^{2-}, the growth of crystals and the anatase to rutile phase transformation were both suppressed. One-hundred percent anatase with a crystallite size of 54 Å and 90% anatase with a crystallite size of 81 Å were present in the TiO_2/SO_4^{2-} catalysts calcined at 300 and 500°C, respectively. In addition, the formation of a bulk titanium sulfate crystal phase was not observed in any of the sulfated samples.

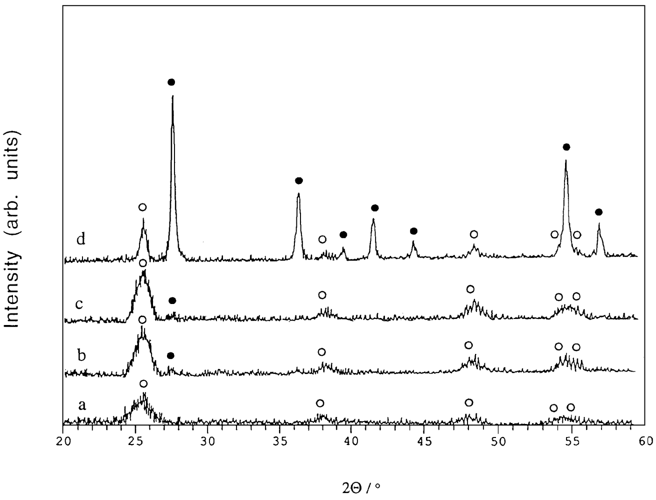


FIG. 1. X-ray diffraction patterns of TiO_2 and TiO_2/SO_4^{2-} calcined at different temperatures for 3 h: (a) TiO_2/SO_4^{2-} (300°C), (b) TiO_2 (300°C), (c) TiO_2/SO_4^{2-} (500°C), and (d) TiO_2 (500°C). (○) anatase; (●) rutile.

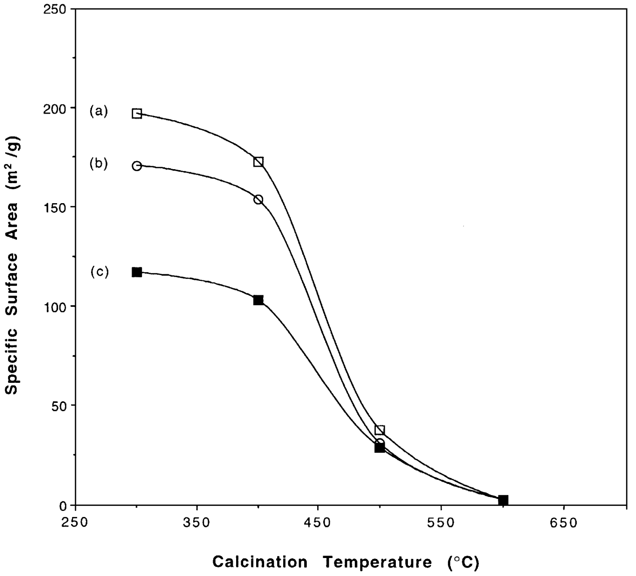


FIG. 2. Effect of calcination and reaction with CFC-12 on the surface area of the TiO_2 catalysts: (a) TiO_2 calcined at the corresponding temperature for 3 h, (b) TiO_2 of curve a recalcined at 300°C for 5 h, and (c) TiO_2 of curve a used for CFC-12 reaction at 300°C for 5 h. Curves b and c were obtained from separate samples of catalyst.

In addition, the XRD measurements indicate that, even after a 5-h reaction with CFC-12 at 300°C, only a slight change in the phase composition of TiO_2 or sulfated TiO_2 catalysts could be detected. However, significant increases in the average crystallite size were found for the samples calcined at 300°C (from 71 to 94 Å and 54 to 73 Å for the TiO_2 and TiO_2/SO_4^{2-}, respectively). Moreover, we could detect no crystalline halide phase in any of the catalysts after reaction with CFC-12.

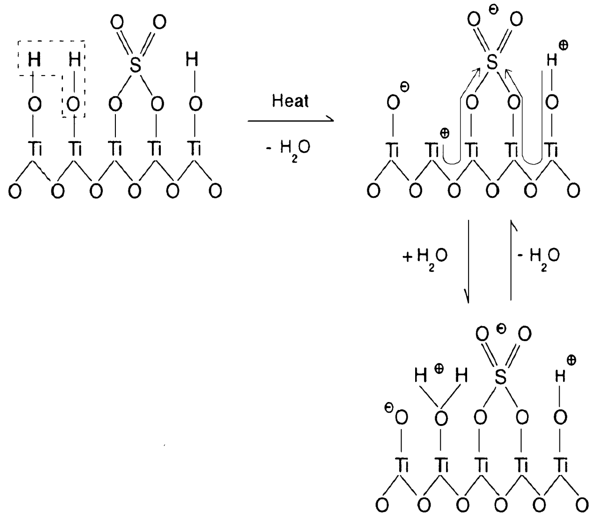
Surface area and pore structure. Structural stability of the TiO_2 and TiO_2/SO_4^{2-} catalysts was studied by examining the influence of thermal treatment under calcination or reaction conditions on the specific surface area and pore size distribution of the catalysts. The results in Fig. 2 show that the specific surface area of the sol-gel-derived TiO_2

decreased with increasing calcination temperature, with a dramatic decrease in specific surface area occurring at ca. 400°C (Fig. 2, curve a). In addition, TiO_2 samples were not stable with respect to the CFC-12 reaction. A ca. 40% decrease in surface area (Fig. 2, curve c) with a significant increase in pore size (Figs. 3a and 3b) was observed for the samples calcined at temperatures lower than 400°C after being used for the CFC-12 reaction at 300°C for 5 h. Even for the TiO_2 sample calcined at 500°C, a 24% loss in specific surface area was still obtained after the reaction. These results are consistent with the XRD observation that the average crystallite size increased greatly after the reaction.

In order to separate the effects of the thermal treatment (300°C, 5 h) and the CFC-12 reaction on the structure of the used catalysts, TiO_2 catalysts that were fired in air at given temperatures for 3 h (labeled "fresh" in Fig. 3) were calcined again in air without CFC-12 at 300°C for 5 h (labeled "refired" in Fig. 3) and then were characterized (Fig. 2, curve b, and Figs. 3a–3c). Separate samples of TiO_2 that were fired in air at given temperatures for 3 h were reacted with CFC-12 at 300°C for 5 h (labeled "used" in Fig. 3) and then were characterized (Fig. 2, curve c and Figs. 3a–3c). The results indicate that, although the thermal treatment may cause some change in surface area and pore size distribution, the CFC-12 reaction is mainly responsible for the dramatic structural changes of the used TiO_2 catalysts. Such dramatic decreases in the specific surface area of TiO_2 catalysts used for the CFC-12 reaction were also reported by Karmakar and Greene (7). In their study, a 75% reduction in catalyst surface area was observed after 4 days of operation at 300°C. Most of this reduction (50%) took place during the initial 1–1.5 h.

The sulfation of TiO_2 greatly retarded the sintering process of TiO_2/SO_4^{2-} during calcination. The TiO_2/SO_4^{2-} catalyst calcined at 500°C had about 3.6 times more surface area (compare Fig. 4, curve b, and Fig. 2, curve a) and a smaller crystallite and pore size (compare Figs. 3c and 3e) than the corresponding pure TiO_2 sample. More importantly, the TiO_2/SO_4^{2-} catalyst calcined at 500°C showed much better structural stability during thermal treatment and reaction with CFC-12 than the pure TiO_2 catalyst. After 5 h of reaction at 300°C, no significant changes in either specific surface area or pore size distribution were observed (Fig. 4, curve b, and Fig. 3e) for the TiO_2/SO_4^{2-} catalyst.

Surface composition and properties. Several pure or H_2SO_4 modified TiO_2 samples, either fresh or after use for CFC-12 hydrolysis under different reaction conditions, were characterized using XPS and FTIR techniques. The XPS results in Fig. 5 show that for pure TiO_2 a binding energy of 458.6 eV was obtained for $Ti_{2p3/2}$, referenced to the C_{1s} level at 284.6 eV. The $Ti_{2p3/2}$ binding energy of the TiO_2/SO_4^{2-} samples shifted to a higher value of 459.1 eV, indicating a very strong interaction between the sulfate anion and titanium cation with increased positive polarity on the titanium cation. This result is consistent with the model of acid sites on solid superacids of sulfated metal oxides as shown in Scheme 1 (28, 32).



SCHEME 1

As expected, the characteristic bidentate sulfate ion structure in our sulfated TiO_2 samples was confirmed by the XPS result that the S_{2p} binding energy was 168.8 eV, attributed to S^{+6} (20, 33), and by FTIR results (Fig. 6) showing the characteristic stretching frequencies of bidentate SO_4^{2-} coordinated to metals such as Ti^{4+} in the 1240–940 cm^{-1} region (15, 20). Further XPS studies indicated that the surface sulfur content of the TiO_2/SO_4^{2-} catalyst calcined at 500°C, as indicated by the XPS intensity ratio of I_{S2p}/I_{Ti2p}, was constant through 5 h of reaction at temperatures $\leq$300°C (Fig. 7, curve b). This constant ratio demonstrates that the surface sulfate species of the catalyst are very stable during both thermal treatment and exposure to the corrosive products of the CFC-12 decomposition reaction throughout the whole range of reaction temperatures employed. It is likely that the improved stability of the TiO_2/SO_4^{2-} catalyst when compared to the TiO_2 catalyst in regard to surface area and pore structure, as discussed in the previous section, can also be ascribed to the formation of surface sulfur complexes (15, 32). These complexes appear to be thermally stable to ca. 500–600°C in an oxidizing atmosphere.

Surface fluorination of a TiO_2 catalyst during the CFC-12 decomposition reaction was reported by Karmakar and Green (7). They found that the surface fluorination was responsible for the loss in surface area, the increase in acidity, and the consequent increase in the initial activity of their TiO_2 catalyst. In our study, similar results were obtained for the pure TiO_2 sol-gel-derived catalyst. Significant surface fluorination was detected by XPS for the TiO_2 catalysts used for the reaction at 300°C and higher temperatures (Fig. 7, curve a). Likewise, the activity of the TiO_2 catalyst (Fig. 8, curve a) increased greatly with increasing reaction

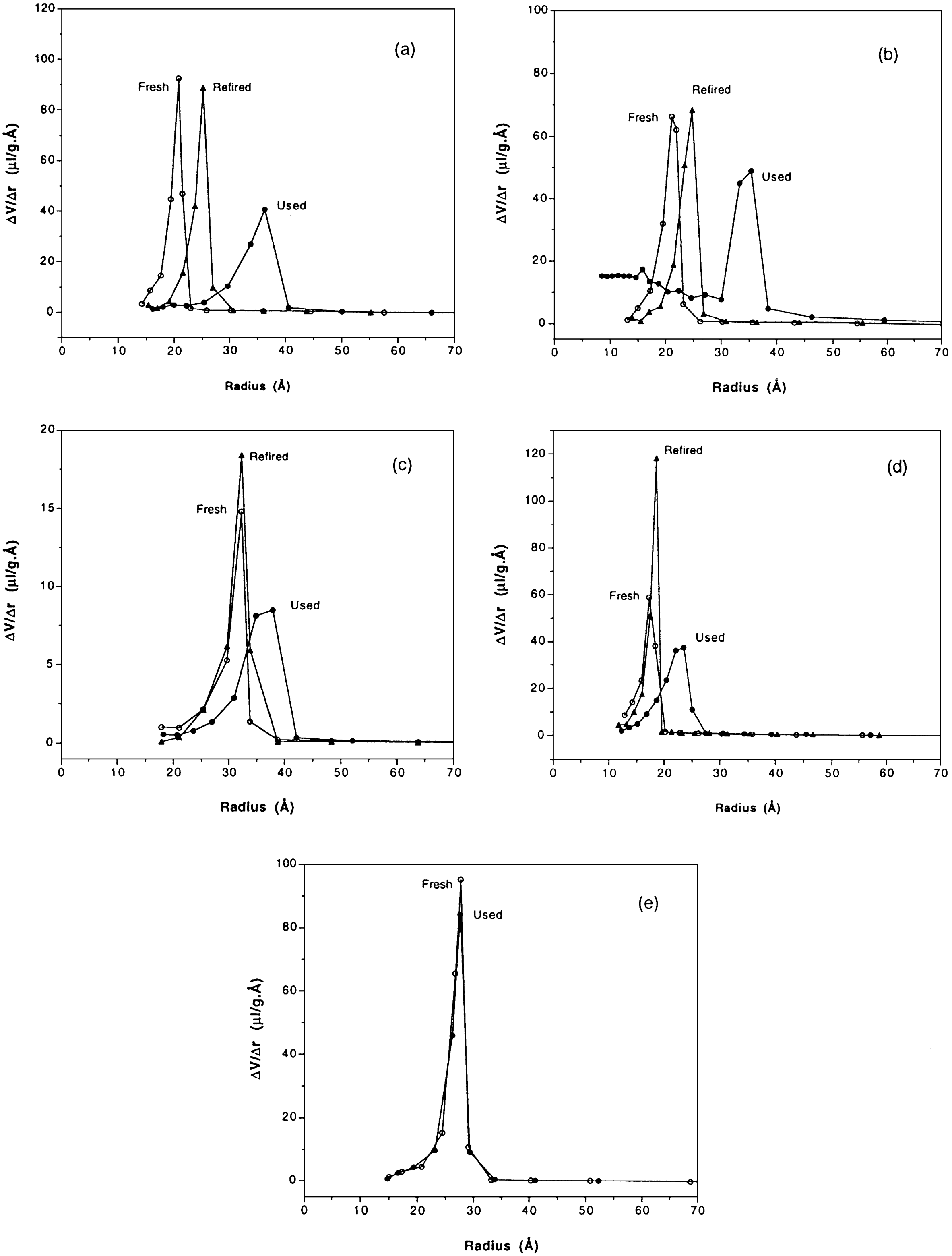


FIG. 3. Effect of calcination and reaction with CFC-12 on the pore size distribution of the TiO_2 and TiO_2/SO_4^{2-} catalysts: (a) TiO_2 (300°C), (b) TiO_2 (400°C), (c) TiO_2 (500°C), (d) TiO_2/SO_4^{2-} (300°C), and (e) TiO_2/SO_4^{2-} (500°C). (○) "fresh," catalyst fired at the corresponding temperature for 3 h; (▲) "refired," catalyst fired at the corresponding temperature for 3 h and refired at 300°C for 5 h; (●) "used," catalyst fired at the corresponding temperature for 3 h and used for reaction with CFC-12 at 300°C for 5 h.

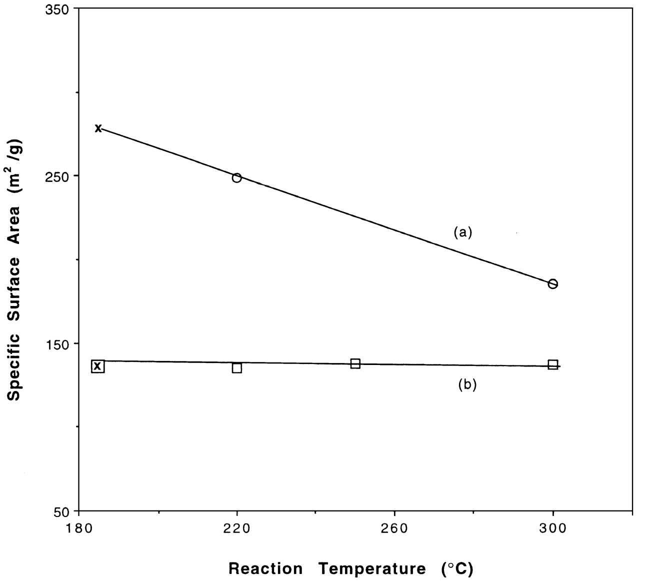


FIG. 4. Effect of calcination and CFC-12 reaction temperature on the surface area of TiO_2/SO_4^{2-} catalysts: (a) TiO_2/SO_4^{2-} calcined at 300°C for 3 h and (b) TiO_2/SO_4^{2-} calcined at 500°C for 3 h. (×) TiO_2/SO_4^{2-} (300°C) without reaction; (☒) TiO_2/SO_4^{2-} (500°C) without reaction.

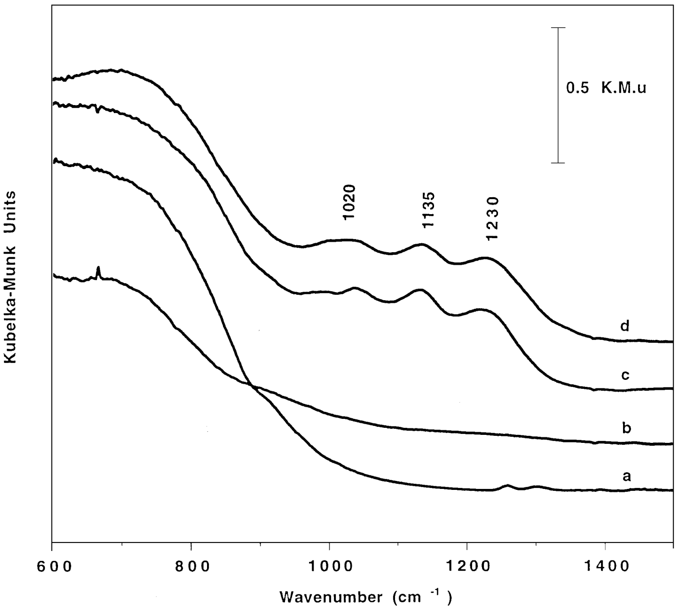


FIG. 6. Diffuse reflectance FTIR spectra of (a) TiO_2 (300°C), (b) TiO_2 (500°C), (c) TiO_2/SO_4^{2-} (300°C), and (d) TiO_2/SO_4^{2-} (500°C).

time (i.e., fluorination time) in the first 3 h. However, for the TiO_2/SO_4^{2-} catalysts, surface fluorination was greatly retarded through sulfation. The surface fluorine content, as indicated by the XPS intensity ratio of I_{F1s}/I_{Ti2p}, was almost constant over the reaction temperature range from 220 to 300°C at a level that was only ca. 1/3 of the saturated fluorine content of the pure TiO_2 catalyst (Fig. 7, curve c). In addition, no improvement in the catalytic activity of the sulfated TiO_2 was observed with increasing reaction time (Fig. 8, curve b). These results indicate that surface fluorination was not involved in the formation of reaction sites for the TiO_2/SO_4^{2-} catalysts. Moreover, the high structural stability and the fact that we could not detect any fluorine-containing by-products (see next section in detail) when using the sulfated catalysts may be ascribed to the low surface

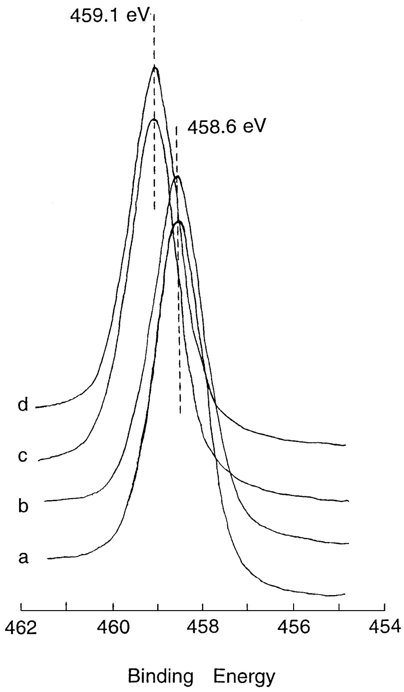


FIG. 5. Titanium XPS spectra ($Ti_{2p3/2}$) of (a) TiO_2 (500°C), (b) TiO_2 (500°C) after reaction with CFC-12 at 350°C, (c) TiO_2/SO_4^{2-} (500°C), and (d) TiO_2/SO_4^{2-} (500°C) after reaction with CFC-12 at 220°C.

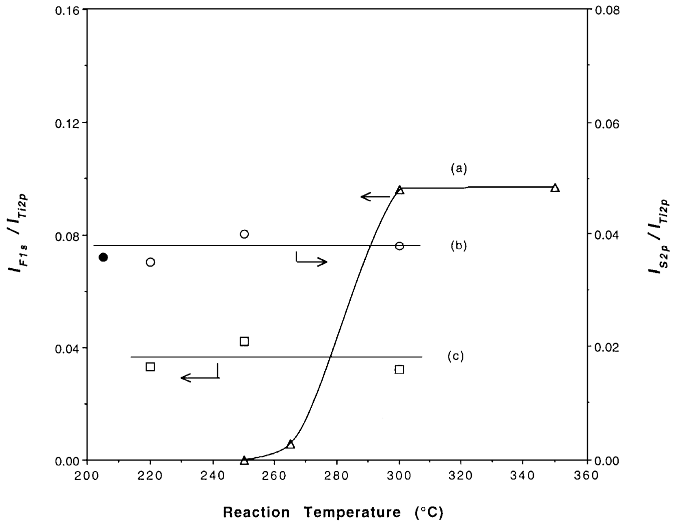


FIG. 7. XPS intensity ratios of I_{F1s}/I_{Ti2p} and I_{S2p}/I_{Ti2p} as a function of reaction temperature for (a) TiO_2 (500°C) and (b) and (c) TiO_2/SO_4^{2-} (500°C). (●) TiO_2/SO_4^{2-} (500°C) without reaction.

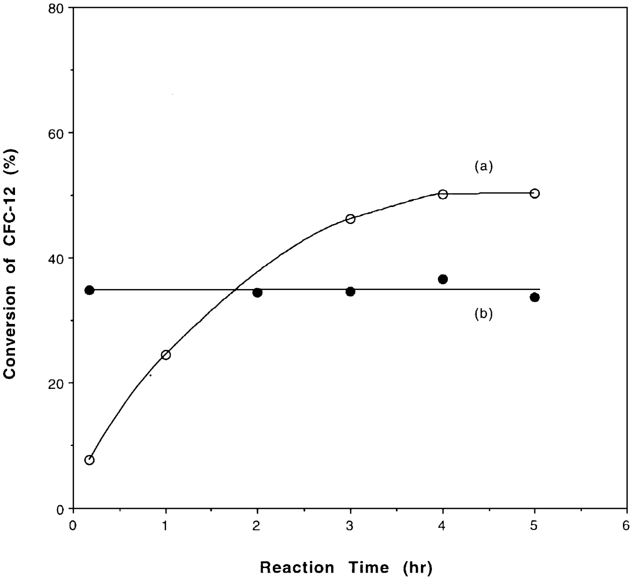


FIG. 8. Conversion of CFC-12 (a) on the pure TiO_2 catalyst at 300°C and (b) on the TiO_2/SO_4^{2-} catalyst at 220°C as a function of reaction time. Both catalysts were calcined at 500°C. A conversion of 100% corresponds to an observed reaction rate of 6.8×10^{-8} mol s^{-1} g^{-1}.

fluorination of the catalyst under the reaction conditions employed.

The acidity and acid strength of sulfated TiO_2 catalysts have been well studied (19, 20, 32). In general, a considerable number of Brønsted and Lewis acid sites are formed by modifying TiO_2 with H_2SO_4. In terms of the Hammett acidity parameter, H_0, the acid strengths of these modified catalysts are typically more negative than −14.5, which makes these catalysts stronger than 100% H_2SO_4 ($H_0 = -11.93$). Formation of such superacid sulfated TiO_2 catalysts has been attributed to the inductive effect of the S=O bonds of the surface sulfate complex (see Scheme 1). These superacid properties have been considered to be responsible for the high catalytic activity of catalysts modified with sulfuric acid in various acid-catalyzed reactions such as the skeletal isomerization of butane, ring-opening isomerization of cyclopropane, alkylation of benzene derivatives, cracking of paraffins, and dimerization of ethylene (22–28). For the catalytic decomposition of CFC-12, it has been established that acid properties of the catalyst correlate well with its activity. Only a strongly acidic site with H_0 more negative than −5.6 was effective in decomposing CFC-12 (9). Therefore, the tremendous increase in activity for CFC-12 decomposition obtained by modifying TiO_2 with H_2SO_4 (see next section for detail) may be attributed to the superacid properties of the sulfated catalysts.

Effect of Sulfation on the Catalytic Properties of the Catalyst

Activity. Figure 9 shows the temperature profile for the decomposition of CFC-12 on pure TiO_2 and H_2SO_4-promoted TiO_2 catalysts calcined at 500°C. The dramatic difference in catalytic activity between the pure TiO_2 and TiO_2/SO_4^{2-} catalysts is indicated by the completely different reaction temperature regions (Fig. 9). For the pure TiO_2 catalyst, the order in which the reaction temperature was changed (i.e., from low to high or from high to low temperature) exerted significant influence on the activity of the catalyst. When the reaction temperature increased from low to high temperature (Fig. 9, curve a), the TiO_2 catalyst was activated at temperatures above 265°C, with 100% conversion of CFC-12 achieved at ca. 345°C and higher. After this catalyst was used for the reaction at the highest temperature (350°C) for 3.5 h, the same catalyst was then employed as the reaction temperature was decreased from high to low (Fig. 9, curve b). It was found that when the TiO_2 catalyst was used with decreasing temperatures (curve b), the catalyst was much more active than when it was used with increasing temperatures (curve a) over corresponding reaction temperatures, especially in the lower temperature region. Moreover, after being used at higher reaction temperatures, the TiO_2 catalyst was still active at ca. 240°C rather than requiring temperatures above 265°C to be activated. This increased activity can be ascribed to the surface fluorination of the catalyst which in turn increases the acidity of the catalyst. A fluorine substitution mechanism that explains this generation of stronger acid sites for the TiO_2 catalyst has been proposed (7).

However, surface fluorination of the TiO_2/SO_4^{2-} catalyst did not have a significant influence on the activity of this

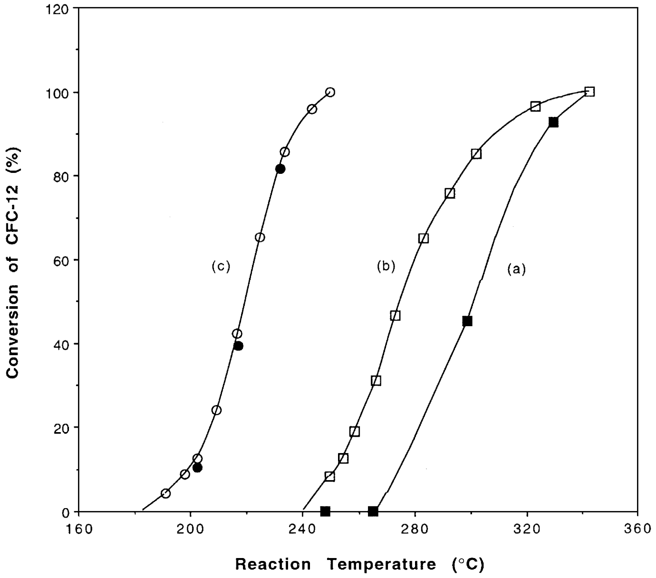


FIG. 9. Effect of reaction temperature on the conversion of CFC-12 with the TiO_2 (500°C) and TiO_2/SO_4^{2-} (500°C) catalysts. (a) TiO_2, reaction temperature from low to high, (b) TiO_2, reaction temperature from high to low, and (c) TiO_2/SO_4^{2-}, reaction temperature from low to high (●) and from high to low (○). A conversion of 100% corresponds to an observed reaction rate of 6.8×10^{-8} mol s^{-1} g^{-1}.

catalyst (Fig. 9, curve c), suggesting that the acid sites generated by surface fluorination do not have enough strength to allow the CFC-12 hydrolysis reaction to take place at low temperatures (<240°C). Superacidity is the likely origin of this surprising high activity of the TiO_2/SO_4^{2-} catalyst at these low reaction temperatures (Fig. 9, curve c). This suggestion was further confirmed by the fact that no obvious activities were observed for HNO_3/TiO_2 and H_2SO_4/C catalysts under the same reaction conditions employed for the sulfated TiO_2 catalyst. For the TiO_2/SO_4^{2-} catalyst, the reaction commences at only 185°C and the complete decomposition of CFC-12 was obtained at 250°C.

Selectivity. It has been demonstrated that, on TiO_2 (7) or TiO_2/SO_4^{2-} (14) catalysts, CFC-12 can be hydrolyzed quantitatively under certain reaction conditions in accordance with the equation

$$CCl_2F_2 + 2H_2O \rightarrow CO_2 + 2HCl + 2HF. \qquad [2]$$

We investigated the influence of reaction temperature on the selectivity to CO_2 of the CFC-12 decomposition on pure or H_2SO_4-promoted TiO_2 catalysts (Fig. 10). The results showed that the TiO_2/SO_4^{2-} catalyst had much higher selectivity for forming CO_2 than the pure TiO_2 catalyst. On both catalysts, the selectivity to CO_2 (defined as the ratio of moles of CO_2 produced to moles of CFC-12 decomposed) increased with increasing reaction temperature. Complete hydrolysis of CFC-12 (i.e., a ratio of 1) was obtained at 250°C on the TiO_2/SO_4^{2-} catalyst. Although 100% conversion of CFC-12 was observed at temperatures above 340°C, complete hydrolysis of CFC-12 was never achieved in the reaction temperature range of 250–350°C over the pure TiO_2 catalyst (selectivity to CO_2 varied from 0.5 to 0.88). It has been verified that $CClF_3$ (CFC-13) was the main byproduct during the decomposition of CFC-12 on the pure TiO_2 catalyst. In addition, CFC-13 was formed only when the TiO_2 surface was fluorinated, indicating that surface fluorine may be involved in forming reaction sites on the TiO_2 catalyst. Under these reaction conditions, CFC-13 was more stable than CFC-12, even though at 350°C CFC-13 still could not be completely hydrolyzed. In contrast, no CFC-13 could be detected over the entire range of reaction temperatures employed when using TiO_2/SO_4^{2-} as the catalyst, and surface fluorination had no influence on the selectivity of the sulfated catalyst. In fact, the only detectable by-product in the effluent was a trace amount of carbon monoxide when using the TiO_2/SO_4^{2-} catalyst under conditions of incomplete hydrolysis (<250°C). The improvement in selectivity obtained by sulfating the TiO_2 substrate may be ascribed to the formation of superacid sites on which the reaction occurred.

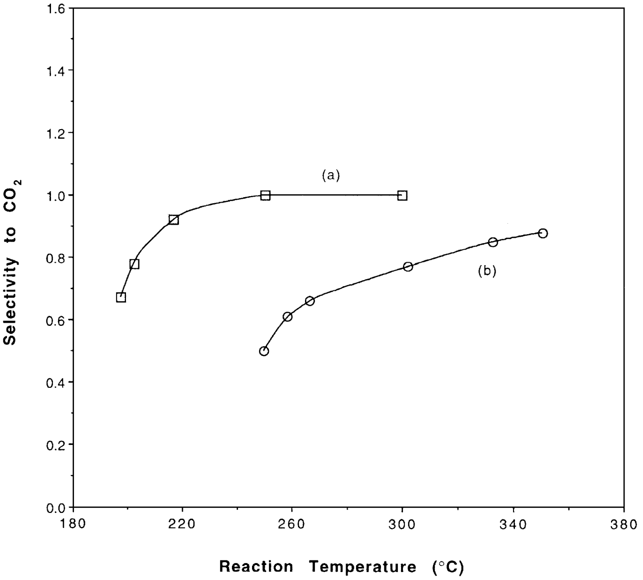


FIG. 10. Effect of reaction temperature on the selectivity to CO_2 for the decomposition of CFC-12 with (a) TiO_2/SO_4^{2-} (500°C) and (b) TiO_2 (500°C) catalysts.

ACKNOWLEDGMENTS

The authors thank Dr. I. Tejedor for the FTIR analyses. Funding for this research was provided by grants from the Water Resources Center, the Graduate School of the University of Wisconsin–Madison, and the Industrial and Economic Development Program of the State of Wisconsin.

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