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# Decomposition of $CCl_2F_2$ over metal sulfate catalysts

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**Abstract**

Activity for hydrolysis of $CCl_2F_2$ (CFC12) on various metal sulfate was investigated. $Zr(SO_4)_2$ was found to be the most active while $FeSO_4$, $Cr_2(SO_4)_3$, $Al_2(SO_4)_3$, $La_2(SO_4)_3$ and $Ce_2(SO_4)_3$ had intermediate activity. $MnSO_4$, $CoSO_4$, and $MgSO_4$ showed low activity and $SrSO_4$, $CaSO_4$, and $BaSO_4$ had even less activity. The major carbon containing product was $CO_2$ and small amount of $CClF_3$ and CO were formed over several sulfates. The crystal structure of the sulfates was stable during decomposition of $CCl_2F_2$, and the conversion reached a steady state after initial decrease at 275 °C over $Zr(SO_4)_2$ catalyst. The concentration of surface hydroxyl was larger than that over $AlPO_4$-based catalysts and a reaction mechanism similar to that over $AlPO_4$-based catalysts was proposed.

*Keywords:* $CCl_2F_2$; $AlPO_4$-based catalyst; $Zr(SO_4)_2$ catalyst

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## 1. Introduction

Chlorofluorocarbons (CFCs) are the main cause of the destruction of the ozone layer and furthermore, it has a strong greenhouse effect [1]. In order to protect the environment a simple low-energy CFC decomposition technique required. Various methods for CFCs decomposition have been proposed, e.g., incineration [2], induced plasma [1], cement kiln [3], super critical water [4], the use of chemical reagents such as sodium naphthalenide [5], irradiation with UV, γ-ray, or ultrasonic wave [6] and catalysts.

Among these methods, catalytic decomposition has the advantages of mild reaction conditions and the use to simple apparatus. Many catalysts have been proposed in the literature so far [7–14]. However, in the decomposition of CFCs, mineral acids such as HF and HCl are formed as products, so the deactivation of catalyst occurs reality. Therefore, in addition to high activity, stability, i.e., resistance to HF and HCl, is an important requirement for the decomposition catalyst of CFCs.

Many researchers have been studying the decomposition of CFCs and reported that the decomposition of chlorofluorocarbons (CFCs) in the presence of water vapor produce strong acids such as HCl and HF via reaction (1) [15–29]. In the absence of water vapor, $F_2$ and $Cl_2$ may be formed via reaction (2):

$$CCl_xF_{4-x} + 2H_2O \rightarrow CO_2 + xHCl + (4-x)HF \quad (1)$$

$$CCl_xF_{4-x} + O_2 \rightarrow CO_2 + \frac{x}{2}Cl_2 + \frac{4-x}{2F_2} \quad (2)$$

In general, metal fluorides are thermodynamically more stable than the corresponding chlorides and

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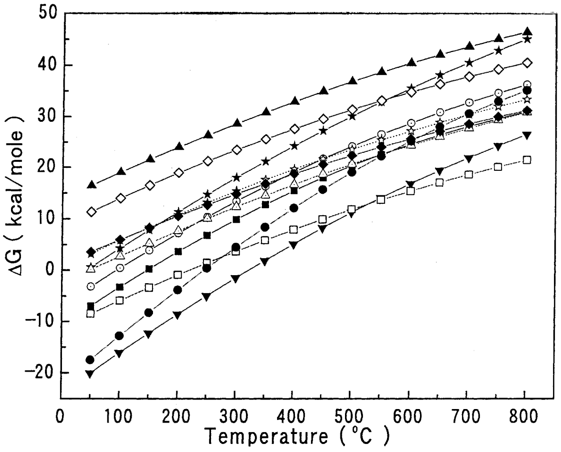

Fig. 1. The $\Delta G$ changes for the reaction $MSO_4 + 2HF \rightarrow MF_2 + H_2SO_4$. One mole of metal basis.

Table 1
Melting points and solubility of some metal sulfates

| Sulfates | Melting point (°C) | Solubility in water |
|---|---|---|
| $Zr(SO_4)_2$ | 100 ($-3H_2O$, 380) | Easy |
| $Al_2(SO_4)_3$ | 770 (decompose) | Easy |
| $La_2(SO_4)_3$ | 1150 | Difficult |
| $Ce_2(SO_4)_3$ | Decompose | Easy |
| $Cr_2(SO_4)_3$ | N/A[a] | Easy: decompose |
| $MnSO_4$ | 700 | Easy |
| $CoSO_4$ | 700 (decompose) | Easy |
| $MgSO_4$ | 1185 | Easy |
| $SrSO_4$ | 1152 | 0.132 g/l |
| $CaSO_4$ | 1193 | Difficult |
| $BaSO_4$ | 1580 | $2.85 \times 10^{-3}$ g/l |
| $Fe_2(SO_4)_3$ | 480 (decompose) | Small: decompose |

[a] Not available.

oxides [15], so metals and metal oxides tend to transform into stable fluorides during the decomposition of CFCs. From this point of view, metals or metal oxides are not suitable catalyst for the $CCl_2F_2$ decomposition. From an evaluation of resistance to fluoridation by HF using thermodynamic data of compounds, the authors selected metal phosphates as catalyst and found that the metal phosphates were effective for the complete decomposition of $CCl_2F_2$ in the presence of water vapor [21]. In particular, $AlPO_4$ and Zr phosphate are active and $CCl_2F_2$ can be decomposed completely over these catalysts temperatures over 350 °C, in the presence of a high concentration of water vapor (about 50 mol%). It was also clarified that the addition of 10 mol% Ce enhanced the catalytic activity [26]. $AlPO_4$ exhibited catalyst life, as expected. Similarly, it was thought that metal sulfates that are thermodynamically well stabilized, should have resistance to fluorination. Fig. 1 shows the $\Delta G$ changes for the reaction between metal sulfate and HF, for example, $MSO_4 + 2HF \rightarrow MF_2 + H_2SO_4$ [30]. It can be seen from the figure that most of the metal sulfates are stable against HF above 300 °C. Generally, metal sulfates have high melting points for example, those of $La_2(SO_4)_3$, $MgSO_4$, $SrSO_4$, $CaSO_4$, $BaSO_4$ are 1150, 1185, 1152, 1193, and 1580 °C, respectively (Table 1). The melting point of Zr $(SO_4)_2$ is also very high but the exact temperature is not known. Melting points of $Ce_2(SO_4)_3$ and $Cr_2(SO_4)_3$ are still not known. Melting point of $Al_2(SO_4)_3$ and $CoSO_4$ are 770 and 700 °C, respectively, but they decompose at these temperatures. Decomposition of CFCs, HFCs, and HCFCs requires the addition of water vapor, therefore sulfates which have the smaller solubility are more suitable as catalysts for CFC decomposition. Generally, most sulfates are soluble in water, but the solubility of $La_2(SO_4)_3$ and $CaSO_4$ is very low. However, low solubility is not necessarily a disadvantage for the catalysts, just like the water-soluble heteropolyacid is practically utilized in oxidation of aldehyde. In this paper, authors investigated the catalytic activity of some metal sulfates for $CCl_2F_2$ decomposition.

## 2. Experimental

### 2.1. Preparation of catalysts

Aluminum sulfate catalyst was prepared by the method described below. An amount of 10 wt.% $NH_4OH$ was added to an aqueous solution of 0.30 M $Al(NO_3)_3 \cdot 9H_2O$ until pH reached 7.0. The $Al(OH)_3$ formed was filtered and washed with pure water. The content of the $Al(OH)_3$ was determined by weighing $Al_2O_3$ formed from calcination of a portion of $Al(OH)_3$ at 1000 °C for 5 h. $Al(OH)_3$ was then dissolved in 5 M $H_2SO_4$ with a small excess of stoichiometric amount. The obtained solution was evaporated to dryness on a hotplate after adjusting pH to 7.0 with $NH_4OH$ solution. The powder obtained was calcined at 400 °C for 5 h and then pressed to cylindrical form, and crushed and 14–32 mesh granules were subsequently collected. Finally it was calcined at 500 °C for 5 h in air.

$Zr(SO_4)_2$ was prepared by the calcination of $Zr(SO_4)_2 \cdot 4H_2O$ (Kishida chemical) at 600 °C for 5 h. Other single metal sulfate catalysts were obtained from commercial source (Wako Pure Chem. Co., pure grade) and they were used for experiments without further purification. The solid materials obtained were pressed, crushed and sieved into 14–32 mesh granules and finally calcined at 600 °C for 5 h in air. Specific surface area before the reaction of the sulfate catalysts, e.g., $Zr(SO_4)_2$, $MnSO_4$, $La_2(SO_4)_3$, and $CoSO_4$ were 8, 6, 2, and 2 $m^2/g$, respectively.

### 2.2. Reactor assembly

The catalytic reactions were carried out under atmospheric pressure using a continuous flow reaction system with a fixed-bed reactor. The details were published elsewhere [21]. The reaction conditions are depicted in the footnotes under the tables. The mixture of $CCl_2F_2$, nitrogen and oxygen was fed into a 16 mm diameter tubular flow reactor made of stainless steel. Water was feed into an evaporator located just above the catalyst bed using a micro-liquid-feeder. The gas effluent from the reactor was washed with distilled water to remove HCl and HF formed. The reaction products were analyzed by Shimadzu GC-8ATP gas chromatograph (thermal conductivity detector, TCD) with a Parapak Q column (4 mm i.d. × 7 m) and a molecular sieve 5A (4 mm i.d. × 3 m) column, and an HP5890GC with HP5970 Mass Spectrometer. Analysis of the products by GC was carried out after 1 h from reaching the required temperature.

The X-ray diffraction patterns (XRD) were measured by a Rigaku RINT-2500HF system. The TPD measurements were carried out in a He flow ($30\ cm^3/min$). $NH_3$ was adsorbed on the sample (1.0 g) that was evacuated at 550 °C for 2 h, at 100 Torr at room temperature for 30 min. After the introduction of He, the desorption was carried out by heating to 550 °C at a constant rate of 10 °C/min. The desorbed gas was detected by TCD and was analyzed by GC-MS (HP 5890 GC with HP 5970 MS). The specific surface areas (SSA) of the fresh and used catalysts were determined by BET method ($N_2$ adsorption) using a Carlo Erba SORPTY-1750 analyzer. Standard concentration of gaseous feed is 0.5 mol% $CCl_2F_2$, 7.5 mol% $O_2$, 34.4 mol% $N_2$, and 57.6 mol% water vapor, and the gas was fed to the catalyst bed at $W/F = 6.73$ g-cat s/cm$^3$.

## 3. Results and discussion

### 3.1. Decomposition of $CCl_2F_2$ over metal sulfate catalysts

Fig. 2 shows the activity of the metal sulfates for the decomposition of $CCl_2F_2$ in the presence of water vapor as a function of temperature. Among the metal sulfates examined, $Zr(SO_4)_2$ exhibited the highest activity for decomposition of $CCl_2F_2$, which began to decompose at around 300 °C. Complete decomposition occurred at 400 °C. The only carbon containing product is $CO_2$. The activity of the $FeSO_4$, $Cr_2(SO_4)_3$, $Al_2(SO_4)_3$, and $La_2(SO_4)_3$ catalysts was lower than that of $Zr(SO_4)_2$. $MnSO_4$, $CoSO_4$, and $MgSO_4$ showed intermediate activity, and $CCl_2F_2$ decomposition proceeded above 400 °C. Catalytic activity of $CaSO_4$ and $SrSO_4$ was found to be very low.

From the temperature at which conversion reached 50%, we tentatively concluded that the order of the activity of the catalysts was $Zr(SO_4)_2 > FeSO_4$,

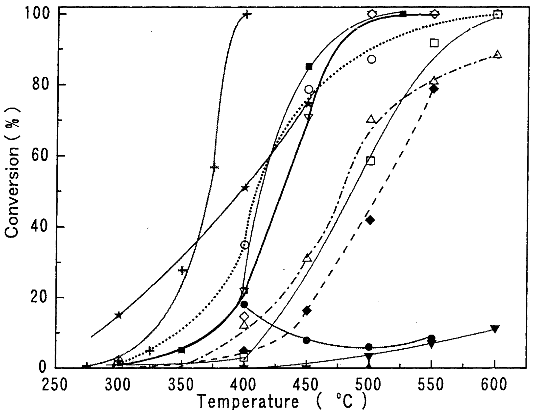

Fig. 2. Catalytic activity of the metal sulfates for the decomposition of $CCl_2F_2$ Catalyst: 4.50 g; feed gas concentration (mol%): $CCl_2F_2$ 0.5, $O_2$ 7.5, $N_2$ 34.4, $H_2O$ 57.6; feed rate: 40 cm$^3$/min. (+) $Zr(SO_4)_2$, (★) $FeSO_4$, (■) $Al_2(SO_4)_3$, (○) $CrSO_4$, (▽) $La_2(SO_4)_3$, (□) $CoSO_4$, (▲) $BaSO_4$, (●) $SrSO_4$, (▼) $CaSO_4$, (◇) $Ce(SO_4)_2$, (△) $MnSO_4$, (◆) $MgSO_4$.

Table 2
Changes in crystal structure during the decomposition of $CCl_2F_2$[a]

| Catalyst | Crystallinity | SSA | (ASTM #), changes during the reaction |
|---|---|---|---|
| $SrSO_4$ | Good | 4 | (80-0523), orthorhombic, no change |
| $MgSO_4$ | Good | 8 | (81-1835), orthorhombic, slightly crystallize |
| $Al_2(SO_4)_3$ | Good | 20 | (81-1835), rhombohedral, slightly crystallize |
| $CaSO_4$ | Good | 4 | (37-1496), anhydrite |
| $BaSO_4$ | Medium | | (76-0213), orthorhombic, slightly decrystallize |
| $Zr(SO_4)_2$ | Medium | 8 → 2 | (24-1492), orthorhombic, no change |
| $MnSO_4$ | Medium | 6 → 8 | $MnSO_4$(35-751) → $MnSO_4$(35-751, 29-898) |
| $LaSO_4$ | Weak | 2 → 1 | $LaSO_4$(39-301) → $LaSO_4$(39-301, 45-904) |
| $Ce_2(SO_4)_3$ | Weak | | Unknown but no $Ce_2(SO_4)_3$ and $CeO_2$ |
| $CoSO_4$ | Medium weak | 2 → 0 | $CoSO_4$(72-1455) → $CoSO_4$(72-1454 > 28-0386) |
| $Cr_2(SO_4)_3$ | Medium weak | | $Cr_2(SO_4)_3$(81-1834), no change |

[a] Catalyst: 5.00 g; feed gas concentration (mol%): 0.5 $CCl_2F_2$, 7.5 $O_2$, 34.4 $N_2$, 57.6 $H_2O$, 40 $cm^3$/min.

$Cr_2(SO_4)_3$, $Al_2(SO_4)_3$ > $La_2(SO_4)_3$, $Ce_2(SO_4)_3$ > $MnSO_4$, $CoSO_4$ > $MgSO_4$ > $SrSO_4$, $CaSO_4$ > $BaSO_4$. Small amount of by-products were formed over several catalysts: $CClF_3$ was formed over $FeSO_4$ (0.38 mol% selectivity at 450 °C), $La_2(SO_4)_3$ (0.8–2.0% at 500–550 °C), $Ce_2(SO_4)_3$ (0.3–0.68% at 500–550 °C), $Mn_2(SO_4)_3$ (1.3–1.6% at 550–600 °C), $CoSO_4$ (0.38–1.3% at 550–600 °C). Carbon monoxide was also formed over $La_2(SO_4)_3$ (2.4% at 500 °C), $Ce_2(SO_4)_3$ (1.1% at 600 °C), and $Mn_2(SO_4)_3$ (1.1% at 600 °C). It is noteworthy that CO formation was observed over these catalysts in contrast to the metal phosphate catalysts [2]. Over metal phosphate catalysts, the essential reaction is hydrolysis of $CCl_2F_2$: $CCl_2F_2 + 2H_2O = CO_2 + 2HCl + 2HF$. Formation of CO may suggest that the following reactions occur over the sulfate catalysts:

$$CCl_2F_2 + \frac{1}{2}O_2 \rightarrow CO + Cl_2 + F_2$$

or

$$CCl_2F_2 + H_2O \rightarrow CO + Cl_2 + 2HF$$

Structure of the catalysts as measured by XRD and specific surface area (SSA) of the sulfate catalysts is shown in Table 2. The sulfate samples before reaction were pure crystal sulfates with the exception of $Ce_2(SO_4)_3$. Crystallinity of $SrSO_4$, $MgSO_4$, and $Al_2(SO_4)_3$ were very high followed by $BaSO_4$, $Cr_2(SO_4)_3$, $Zr(SO_4)_2$, and $MnSO_4$. Crystallinity of $CoSO_4$, $La_2(SO_4)_3$, and $FeSO_4$ were significantly low but it was sufficient for isolation of the crystal phase. The structure of the cerium sulfate could not be identified by XRD, but it was not $Ce_2(SO_4)_3$ or $CeO_2$ (Fig. 3). The structure of some sulfates was changed slightly during the decomposition of $CCl_2F_2$. $MnSO_4$, $CoSO_4$, and $La_2(SO_4)_3$ were partly changed to another crystal phase of each sulfate.

SSA of sulfates was generally small, in the range of 2–8 $m^2$/g, with the exception of $Al_2(SO_4)_3$ (20 $m^2$/g). SSA decreased during decomposition of $CCl_2F_2$: from 8 to 2 $m^2$/g for $Zr(SO_4)_2$, from 2 to less than 1 $m^2$/g for $La_2(SO_4)_3$ and $CoSO_4$, respectively. Only the SSA of $MnSO_4$ increased from 6 to 8 $m^2$/g during the decomposition. The decrease in activity at higher temperatures cannot be explained by the crystallization of the catalyst. It is not clear at this stage.

On the other hand, $CaSO_4$, $SrSO_4$ and $BaSO_4$ catalysts are salts of strong bases and strong acid, so the acidity of these sulfates is thought to be small. Small SSA may account for the low activity of these sulfates for $CCl_2F_2$ decomposition.

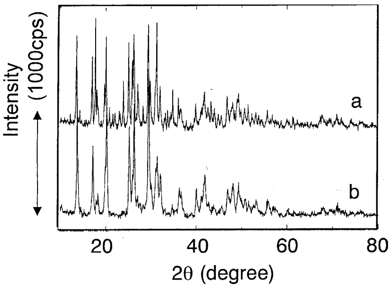

Fig. 3. XRD patterns of $Ce_2(SO_4)_3$: (a) after the reaction; (b) before reaction.

Crystal structure of the sulfates was not changed during the catalytic decomposition of $CCl_2F_2$, except for $MnSO_4$. Therefore, it can be concluded that metal sulfates are generally stable under the reaction conditions of decomposition of $CCl_2F_2$, as expected from Gibbs free energy changes. $Zr(SO_4)_2$ was the most active among the examined metal sulfates and its activity is almost the same as that of $AlPO_4$. In conclusion, most of the metal sulfates, in particular $Zr(SO_4)_2$, are effective for $CCl_2F_2$ decomposition.

### 3.2. Effect of concentration of reactants

Decomposition of $CCl_2F_2$ over $Zr(SO_4)_2$ was studied further to understand the reaction mechanism. The essential reaction of $CCl_2F_2$ decomposition over metal phosphates is hydrolysis, as reported in [24]. The essential reactions over metal sulfates are thought to be hydrolysis, since they are salts similar to phosphates. Therefore, the effects of concentration of reactants on the decomposition were studied. Fig. 4 shows the conversion of $CCl_2F_2$ on $Zr(SO_4)_2$ as a function of $H_2O$ concentration. Under dry atmosphere, conversion of $CCl_2F_2$ was as low as 32% at 300 °C, and CO, $CClF_3$ (10% selectivity), and a small amount of dimer were formed in addition to $CO_2$. On the other hand, addition of 5.0 mol% $H_2O$ drastically increased the conversion of $CCl_2F_2$ and only $CO_2$ was formed. Catalytic activity was decreased by the further increase in $H_2O$ concentration. Although the reaction rates cannot be compared at the same reaction temperature, reactivity of $CCl_2F_2$ increased with the increase of water vapor concentration up to 5 mol%, thus suggesting that the essential reaction is hydrolysis. Decrease of catalytic activity at high water concentration may be due to the inhibition of adsorption of $CCl_2F_2$ by adsorption of the water molecule. Optimum concentration of water vapor seems to be about 5% for decomposition of 0.5 mol% $CCl_2F_2$.

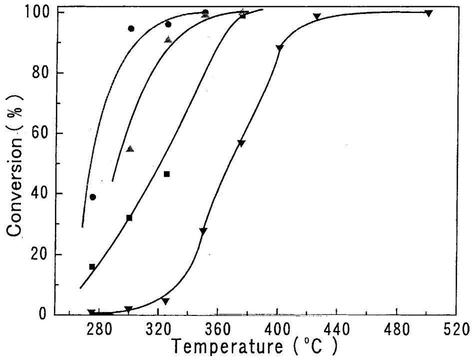

Fig. 4. Effect of $H_2O$ concentration on the decomposition of $CCl_2F_2$. Catalyst: $Zr(SO_4)_2$ 4.50 g; feed gas concentration (mol%): $CCl_2F_2$ 0.5, $O_2$ 18.9, $N_2$ balance; feed rate: 40 cm$^3$/min.

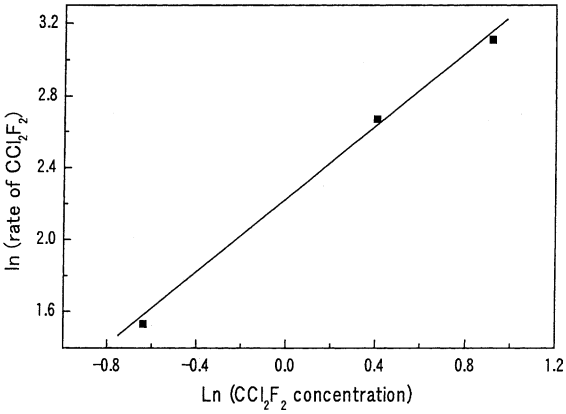

Fig. 5. Effect of $CCl_2F_2$ concentration on the decomposition rate on $CCl_2F_2$.

The concentration of oxygen had less influence on the conversion over a wide range of oxygen concentration. This supports the view that essential reaction of decomposition of $CCl_2F_2$ over $Zr(SO_4)_2$ is hydrolysis.

The effects of $CCl_2F_2$ concentration on the rate of $CCl_2F_2$ decomposition at 275 °C were studied. Reaction rate increased with the increase of $CCl_2F_2$ concentration and reaction temperature. Logarithmic reaction rates are plotted against logarithmic $CCl_2F_2$ concentrations in Fig. 5. A good linear relationship was obtained and the slope was about unity. This suggests that the rate determining step is the adsorption of $CCl_2F_2$ or the surface reaction of adsorbed species derived from $CCl_2F_2$ in the standard reaction conditions of this study.

### 3.3. Stability of the sulfate catalyst

The effect of reaction time on the $CCl_2F_2$ conversion was studied over $Zr(SO_4)_2$ at 275 °C to clarify the stability of the sulfate catalysts. As shown in Fig. 6, conversion decreased with the time on stream for the first 15 h but thereafter it seemed to be constant. The

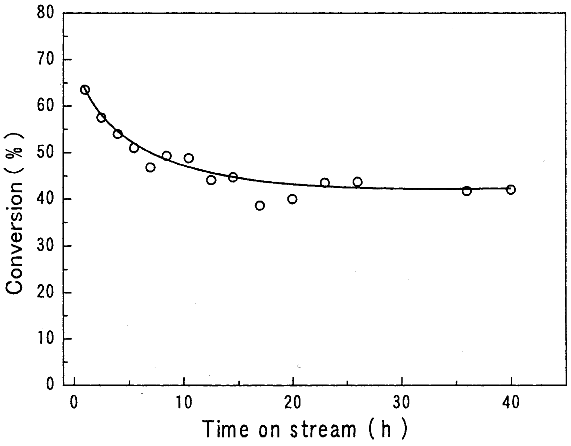

Fig. 6. The effect of reaction time on the $CCl_2F_2$ conversion. $Zr(SO_4)_2$: 4.50 g; reaction temperature 275 °C; feed gas concentration (mol%): $CCl_2F_2$ 0.5, $O_2$ 18.9, $N_2$ balance; feed rate: 40 $cm^3/min$.

time required for stabilization of the activity was 15 h. It is somewhat shorter than that of $AlPO_4$. This may be due to differences in the water vapor concentration. The structure of the catalyst analyzed by XRD was not changed after reaction for 40 h. The specific surface area of the catalyst decreased from 8 to 2 $m^2/g$ at the initial state; the gradual decrease in the conversion may be due to this decrease of surface area of the catalysts. It can be concluded that the zirconium sulfate is stable under the reaction conditions, decomposition of $CCl_2F_2$ and it is expected that the activity of the catalyst for $CCl_2F_2$ hydrolysis will be sustained over longer periods.

### 3.4. TPD spectra of water vapor adsorbed on $Zr(SO_4)_2$

Several researchers have suggested that the acid sites on the catalysts play an important role in CFC decomposition. The authors also studied CFC decomposition over $AlPO_4$ catalysts containing Ce as a promoter and found that $AlPO_4$ catalysts containing Ce are the mixture of $CePO_4$ and $AlPO_4$. These catalysts have acid sites and the addition of Ce to $AlPO_4$ reduced the number of acid sites in catalysts. The catalytic activity for CFC decomposition, however, increases with the addition of 10 mol% of Ce. This shows that the catalytic activity for CFC decomposition is not proportional to the acidity of the catalysts. Authors compared the adsorbed amounts of water vapor for the $AlPO_4$ catalyst and Ce containing $AlPO_4$ catalyst and found that the absolute amount of water vapor on the $AlPO_4$ is larger than that on $CePO_4$–$AlPO_4$ (Ce/Al = 1/9), the concentration of surface OH group on the $CePO_4$–$AlPO_4$ catalyst is larger than that on $AlPO_4$. If, on the surface one OH group reacts with $CCl_2F_2$ molecule to form surface species, catalytic activity should be proportional to the absolute amount of surface hydroxyl group. Since the catalytic activity is not proportional to the absolute amount but the concentration, we proposed a bidentate surface species as depicted in Fig. 7 for a surface intermediate [31].

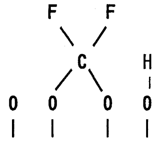

Fig. 7. Estimated surface species derived from $CCl_2F_2$.

From this viewpoint, TPD of water vapor on the $Zr(SO_4)_2$ was studied and the result is shown in Fig. 8 together with the result of $CePO_4$–$AlPO_4$. Desorption of water begins at about 250 °C and reaches a plateau at 300–450 °C and a small peak at around 475 °C. The amounts of desorbed water from both catalysts are summarized in Table 3. The desorbed amount of water from $Zr(SO_4)_2$ was

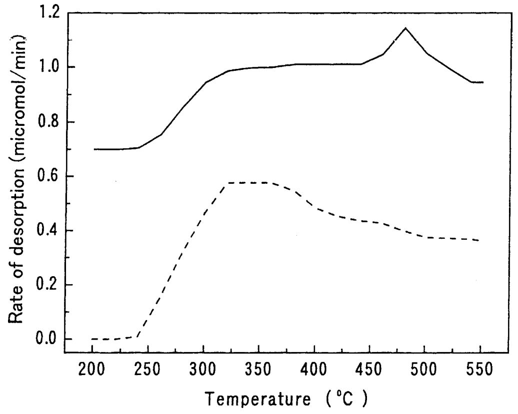

Fig. 8. TPD profile of $H_2O$ on $Zr(SO_4)_2$ and $CePO_4$–$AlPO_4$ (Ce/Al = 1/9). (–––) $Zr(SO_4)_2$, (---) $CePO_4$–$AlPO_4$ (Ce/Al = 1/9).

Table 3
Amounts of surface hydroxyls

| Catalyst | SSA ($m^2/g$) | Desorbed amount | |
|---|---|---|---|
| | | $\mu$mol/g | $\mu$mol/$m^2$ |
| $Zr(SO_4)_2$ | 8 | 88.7 | 11.1 |
| $CePO_4$–$AlPO_4$ | 84 | 135.3 | 1.6 |

smaller than that from $CePO_4$–$AlPO_4$. However, surface area of $Zr(SO_4)_2$ was much smaller than that of $CePO_4$–$AlPO_4$, therefore, the concentration of surface hydroxyls over $Zr(SO_4)_2$ is much higher than that over $CePO_4$–$AlPO_4$. Higher activity of $Zr(SO_4)_2$ similar to $CePO_4$–$AlPO_4$ for $CCl_2F_2$ decomposition may be due to the high concentration of surface hydroxyls.

## 4. Conclusions

(1) Metal sulfates are effective for $CCl_2F_2$ decomposition, especially, $Zr(SO_4)_2$ is very active and $CCl_2F_2$ can be decomposed completely at 300 °C.
(2) Metal sulfates are very stable in the $CCl_2F_2$ decomposition up to 500 °C, except for $Ce_2(SO_4)_3$.
(3) Essential reaction for the $CCl_2F_2$ decomposition is hydrolysis.
(4) Reaction mechanism will be similar to that over metal phosphates via bidentate intermediate.

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