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Journal of Molecular Catalysis A: Chemical 155 (2000) 111–119

JOURNAL OF  
MOLECULAR  
CATALYSIS  
A: CHEMICAL

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# Decomposition of chlorofluorocarbons over metal phosphate catalysis

## II. Origin of the stability of $\text{AlPO}_4$ and the location of Ce as a promoter

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### Abstract

Aluminum-phosphate catalysts prepared from aqueous solution of  $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$  in acidic condition are effective for hydrolysis of  $\text{CCl}_2\text{F}_2$ . Active species of the  $\text{AlPO}_4$  catalysts were studied and it was found that not  $\text{Al}(\text{PO}_3)_3$  but pure  $\text{AlPO}_4$  was active.  $\text{AlPO}_4$  was amorphous when calcined at  $1000^\circ\text{C}$  for 5 h. But a slight crystallization of  $\text{AlPO}_4$  took place after the reaction at  $400^\circ\text{C}$  for 1000 h. Crystallization of  $\text{AlPO}_4$  proceeded only in the presence of both  $\text{CCl}_2\text{F}_2$  and water vapor. Replacement of 5–10 at.% of Al in  $\text{AlPO}_4$  by Ce increased the catalytic activity without changing the selectivity. The Ce-promoted catalysts were composed of the mixture of  $\text{AlPO}_4$  and  $\text{CePO}_4$ . The compositions of the catalysts were the same as those of parent liquor in preparation and it was almost uniform in the surface and the bulk.  $\text{AlPO}_4$  in the Ce-promoted  $\text{AlPO}_4$  catalyst was partially crystallized after the calcination at  $1000^\circ\text{C}$  for 5 h. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Chlorofluorocarbon decomposition; Metal phosphate catalysis;  $\text{AlPO}_4$ ; Promotion effect

### 1. Introduction

Millions of metric tons of chlorofluorocarbons (CFCs) produced so far are still being utilized in the form of refrigerants, solvents, etching and cleaning agents in the electronic industry. Since CFCs are chemically stable, those are diffused to the stratosphere and destroy ozone molecules to oxygen molecules.

Furthermore, CFCs are significantly responsible for the greenhouse effect. Accordingly, many attempts to decompose CFCs completely are carried out. However, a safe, simple and cheap decomposition method still remains to be developed.

So far, it has been found to explore the effective catalysts for CFCs decomposition. A number of catalysts including  $\text{Al}_2\text{O}_3$ , activated charcoal,  $\text{Fe}_2\text{O}_3$ /active charcoal [1],  $\text{SiO}_2$ – $\text{Al}_2\text{O}_3$  [2], H- and Na–Y zeolites, H-mordenite,  $\text{TiO}_2$ – $\text{SiO}_2$ , and  $\gamma$ - $\text{Al}_2\text{O}_3$  [3], 0.5–10 wt.%

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$\text{H}_2\text{SO}_4/\text{TiO}_2$ , 5.0 wt.%  $\text{CuO}/\text{CuSO}_4$  [4],  $\text{BPO}_4$  [5–7],  $\text{Au}/\text{Co}_3\text{O}_4$  [8],  $\text{Au}/\text{Al}_2\text{O}_3$  [9],  $\text{ZnO}$ ,  $\text{WO}_3$ ,  $\text{V}_2\text{O}_5$ , and  $\text{Cr}_2\text{O}_3$  supported on  $\gamma\text{-Al}_2\text{O}_3$  [10,11], and  $\text{WO}_3/\text{Al}_2\text{O}_3\text{-ZrO}_2$  [12],  $\text{FeCl}_3/\text{active charcoal}$  [13], are reported. However, no catalysts which has sufficient catalytic activity, and long catalyst life, have been found. Decomposition generally leads to the formation of hydrogen halides, which are strong acids. HF is especially strong acid and reacts with the components of catalysts to produce fluorides, which bring about deactivation. In previous papers [14–16], the authors reported that  $\text{AlPO}_4$  has high decomposition activity, 100%  $\text{CO}_2$  selectivity, and extremely long catalyst life. For example, 0.5 mol%  $\text{CCl}_2\text{F}_2$  in the feed gas composed of about 50 mol% water vapor and air, is converted completely at  $450^\circ\text{C}$ . To clarify the catalyst life, a long-term experiment was carried out at  $400^\circ\text{C}$  and it was observed that the conversion reached to steady state except for the initial decrease for 50 h. After the 1000-h reaction period, X-ray diffraction (XRD) measurement of the catalyst revealed that  $\text{AlPO}_4$  was partly crystallized and a very small amount of  $\text{AlF}_3$  was present in the catalyst.

Crystallization of active phases is usually related to the activity and the life of catalysts. The effect of water vapor on the crystallization of  $\text{AlPO}_4$ , origin of the  $\text{AlF}_3$  present in the catalyst after reaction and the species of the catalyst are studied this paper.

## 2. Experimental

### 2.1. Preparation of catalysts

Metal phosphate catalysts were prepared by the precipitation method described below. An aqueous solution composed of stoichiometric amounts of metal nitrate and 85% ortho-phosphoric acid, and an aqueous solution of 10 wt.% ammonium hydroxide were simultaneously dropped into a separate vessel keeping the pH of the mixture as 4.5. The precipitate was well

washed by pure water and filtrated. The resulting powder was pressed, crushed, and sieved into 14–32 mesh granules and finally it was calcined at  $1000^\circ\text{C}$  for 5 h in air. The mixed phosphate catalyst was prepared from a mixed solution of Al and Ce nitrates.

### 2.2. Experimental procedure

Catalytic reactions were carried out under an atmospheric pressure using a continuous flow reaction system with a fixed-bed reactor as shown in Fig. 1. The reaction conditions are given in the captions of tables. The mixture of  $\text{CCl}_2\text{F}_2$ , nitrogen and oxygen was fed into a 16-mm diameter tubular flow reactor made of stainless steel. Water was supplied into an evaporator located just above the catalyst bed using a micro-liquid-feeder. The gas effluent from the reactor was slightly washed with distilled water to remove HCl and HF. Analysis of the reaction products was carried out using Shimadzu GC-8ATP gas chromatographs (thermal conductiv-

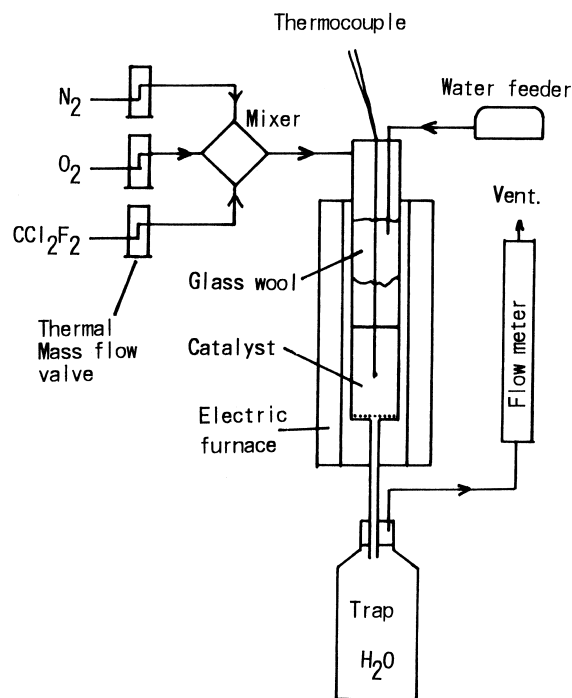


Fig. 1. Schematic diagram of the reaction apparatus.

ity detector, TCD) with a Porapak Q column (4 mm (i.d.)  $\times$  7 m) and a molecular sieves 5A (4 mm id  $\times$  3 m) column, and an HP5890GC with HP5970 Mass Spectrometer. Analysis of the products by GC was carried out 1 h after from reaching the required temperature.

XRD patterns were obtained by a Rigaku RINT 2500HF system. 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.

### 3. Results and discussion

#### 3.1. Active species of the aluminum phosphate catalyst

The aluminum phosphate catalyst which show high catalytic activity was prepared from an aqueous solution of aluminum nitrate and an aqueous solution of ammonia, and it was amorphous after the calcination at 1000°C for 5 h. Two compounds,  $AlPO_4$  and  $Al(PO_3)_3$  have been well known as crystalline aluminum phosphates. To examine the active species of the catalyst, decomposition of  $CCl_2F_2$  was carried out using the mixture of 80 wt.% of crystalline  $Al(PO_3)_3$  and 20 wt.% of the aluminum phosphate catalyst as a binder. No reaction of  $CCl_2F_2$  took place up to 500°C, but about 17.7% of  $CCl_2F_2$  was consumed at 550°C and some CFCs were obtained but no further identification was carried out. The SSA of the crystalline  $Al(PO_3)_3$  is about 24.9 m<sup>2</sup>/g which is much smaller than 160 m<sup>2</sup>/g of the aluminum phosphate catalyst. It can be concluded that  $Al(PO_3)_3$  is not an active species for the decomposition of  $CCl_2F_2$ .

Since the catalyst after a long term reaction gave the defecation peaked due to  $AlPO_4$  and the composition of the aluminum phosphate catalyst determined by the chemical analysis was closely near to Al:P = 1:1, it is reasonable to consider that the active species of the aluminum phosphate catalyst is amorphous  $AlPO_4$ .

#### 3.2. Stability of $AlPO_4$ structure in the presence of water vapor

In a previous paper [15], the authors reported that  $CCl_2F_2$  was decomposed to  $CO_2$ , HCl, and HF over  $AlPO_4$ , and high catalytic activity lasted for 1000 h at 400°C except for an initial decrease for 50 h.

The  $AlPO_4$  catalyst before reaction, which was calcined at 1000°C for 5 h, was amorphous.

After the reaction for 1000 h, small diffraction peaks due to  $AlPO_4$  were observed in the XRD pattern of the catalyst. This suggests that the crystallization of the catalyst took place very slowly. In addition to this, very small diffraction peaks due to  $AlF_3$  also appeared in the spectrum. How was this  $AlF_3$  formed in the catalyst?

It is well known that  $Al_2O_3$  is easily reacted with HF to give  $AlF_3$  [16–18]. So that, there are two possibilities for the  $AlF_3$  formation: one is the  $AlF_3$  formation from  $Al_2O_3$ , which was contained in the catalyst as an impurity, and other is the formation by the reaction between  $AlPO_4$  and HF. The chemical analysis of the catalyst which was used to the catalytic test for 1000 h, revealed that the catalyst had the composition of Al:P = 52.8:47.2. Although various kinds of aluminum phosphates are reported so far, no compounds which have the Al/P ratio higher than unity is not known. It has been reported that precipitates obtained at pH near 7.0 contained a small amount of  $Al_2O_3$  in the preparation of  $AlPO_4$  by precipitation method. Since the catalyst used in this study was prepared at pH = 7, the catalyst may contain  $Al_2O_3$ . If so, the  $Al_2O_3$  may easily be converted into  $AlF_3$  during the reaction. However, all of the detected  $AlF_3$  may not necessarily come from only  $Al_2O_3$ . It has to be proved that  $AlPO_4$  is not changed during the reaction. Consequently, the  $CCl_2F_2$  decomposition was carried out using a pure  $AlPO_4$  catalyst was prepared by the precipitation method at pH = 5.0 when a composition of 50.5 at.% Al. The results are shown in Fig. 2. The conversion was about 90% at the

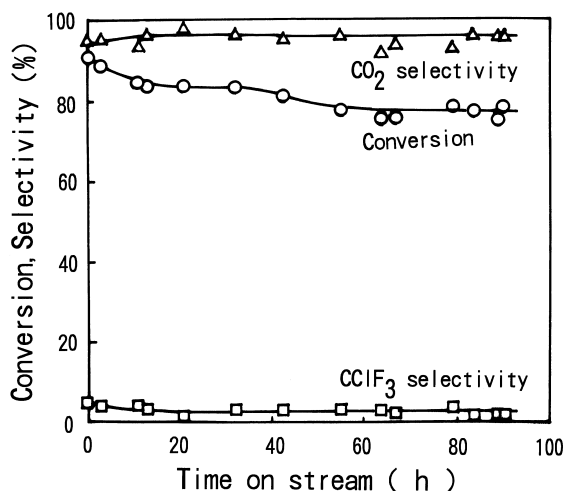


Fig. 2. The effect of time on stream on the  $\text{CCl}_2\text{F}_2$  decomposition over the pure  $\text{AlPO}_4$  catalysts. Catalyst:  $\text{AlPO}_4$  (Al:P = 50.0:49.5) 4.50 g; feed gas rate ( $\text{cm}^3/\text{min}$ ): 0.5  $\text{CCl}_2\text{F}_2$ , 3.0  $\text{O}_2$ , 13.5  $\text{N}_2$ , 22.1  $\text{H}_2\text{O}$ ; reaction temperature:  $400^\circ\text{C}$ .

start of the reaction, which is slightly decreased within initial 50 h, and it reached to take a steady state of about 80%. The XRD patterns of the pure catalyst before and after the reaction are shown in Fig. 3. Most of the catalyst before

reaction is amorphous. After the reaction, a part of  $\text{AlPO}_4$  was crystallized, but no diffraction peaks due to  $\text{AlF}_3$  were observed. In case of the reaction using the catalyst of 52.8% Al, the conversion was decreased from 100% to about 60% within initial 50 h. The closer the stoichiometric composition of the catalyst, the smaller the decrease in the conversion. This suggests that the deactivation be related to the  $\text{AlF}_3$  formation from  $\text{Al}_2\text{O}_3$  existing as impurity in the catalyst. It is believed that the pure  $\text{AlPO}_4$  has never been transformed to  $\text{AlF}_3$  during the  $\text{CCl}_2\text{F}_2$  decomposition.

The  $\text{CO}_2$  selectivity of the catalyst of 50.5 mol% Al was about 96% which was slightly higher than that of 52.8% Al, in other words, the formation of  $\text{CClF}_3$  was promoted over the catalysts containing high concentration of  $\text{Al}_2\text{O}_3$ . This can only be explained if the halogen exchange reaction between  $\text{CCl}_2\text{F}_2$  and F ions of the catalyst was promoted over  $\text{AlF}_3$ . Actually, the promotion of the halogen exchange reaction over metal fluoride catalysts has been reported in the literature [17–23].

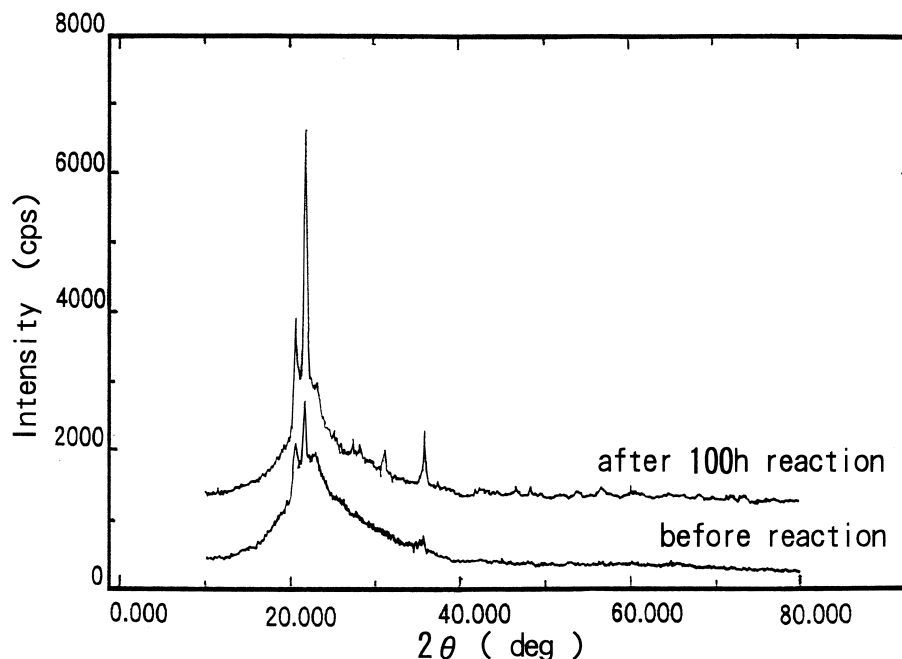


Fig. 3. XRD patterns of the catalyst before and after use for  $\text{CCl}_2\text{F}_2$  decomposition. Catalyst and reaction conditions are the same as given in Fig. 2.

The  $\text{AlPO}_4$  catalysts prepared in this study have significantly large SSA of 120–160  $\text{m}^2/\text{g}$  after the calcination at 1000°C for 5 h. Although the  $\text{AlPO}_4$  catalyst has an advantage of having no reactivity with HF, a slightly crystallization of  $\text{AlPO}_4$  took place during the reaction. In general, progress of the crystallization brings about decrease in SSA, which is connected to the catalytic activity. In this study, decomposition of  $\text{CCl}_2\text{F}_2$  has been carried out under high concentration of water vapor, so that the presence of water vapor may promote the crystallization of  $\text{AlPO}_4$ . In order to examine these hypotheses, heat treatments of the  $\text{AlPO}_4$  catalyst were carried out in the presence of water vapor as high as 50 mol% and in the absence of  $\text{CCl}_2\text{F}_2$ . However, no changes was found in the XRD patterns of the catalyst before and after the treatment at 550°C for 30 h. Although the treatment was carried out at the temperature higher than that of the catalytic reaction, the initial SSA of the catalyst, 125  $\text{m}^2/\text{g}$ , was not changed at all.

It clearly shows that no crystallization of  $\text{AlPO}_4$  takes place due to the presence of water vapor at 550°C. Crystallization can be proceeded in the presence of both  $\text{CCl}_2\text{F}_2$  and water vapor. Although there is no direct evidence for the presence of Al–F and P–F bonds, presence of F ions was detected by XPS. Perhaps F ions formed during the catalytic decomposition may cleave the bridged Al–O–P bonds before removing from  $\text{AlPO}_4$  and this may be responsible for the gradual progress of crystallization.

### 3.3. Optimum concentration of cerium

The effect of various elements as promoter into  $\text{AlPO}_4$  on the catalytic activity was studied and it was found that replacement of 10 at.% Al in  $\text{AlPO}_4$  by Ce brought about a marked improvement on the activity for  $\text{CCl}_2\text{F}_2$  decomposition. Therefore, the authors decided to further investigate the optimum composition of the Ce. The results are shown in Fig. 4. The catalytic

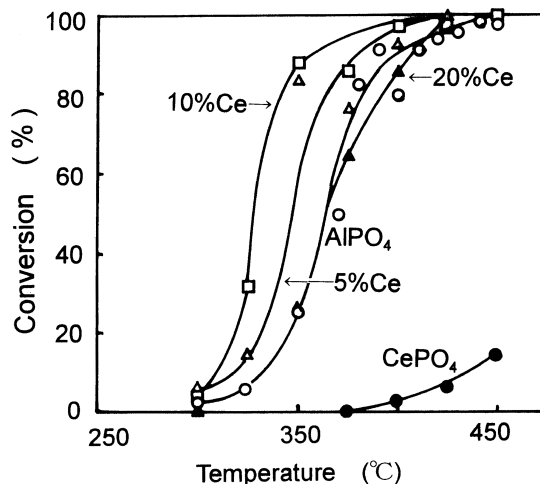


Fig. 4. The effect of Ce content in the  $\text{AlPO}_4$  catalysts on the decomposition activity. Catalyst: 4.50; feed gas rate ( $\text{cm}^3/\text{min}$ ): 0.5  $\text{CCl}_2\text{F}_2$ , 3.1  $\text{O}_2$ , 12.1  $\text{N}_2$ , 19.0  $\text{H}_2\text{O}$ .

activity of the  $\text{AlPO}_4$  catalyst was increased by replacement by 5% Ce, and the conversion curve was shifted to lower temperature by about 20°C. The catalytic activity was further improved by the 10% replacement and the temperature for the same conversion was lowered by 40°C. But the replacement of 20% had no effect in the conversion. The introduction of Ce into the  $\text{AlPO}_4$  catalyst affected only catalytic activity and no influence on the product distribution was observed. It is obvious that 10 at.% Ce is optimum. The results of the catalytic activity of  $\text{CePO}_4$  are also shown in Fig. 4. Catalytic activity of  $\text{CePO}_4$  was so small that the conversion reached only 16% at 450°C.

The SSA of the  $\text{AlPO}_4$  catalyst prepared at pH = 7 is about 118  $\text{m}^2/\text{g}$ , which is somewhat smaller than 140  $\text{m}^2/\text{g}$  of the catalyst prepared at pH = 4.5. With increasing the Ce concentration, SSA of the catalyst is decreased. The SSA of the catalysts containing 10% and 20% Ce is 67 and 43  $\text{m}^2/\text{g}$ , respectively. The SSA of the  $\text{CePO}_4$  catalyst was only 3  $\text{m}^2/\text{g}$ . If the catalysts are composed of simple mixture of  $\text{AlPO}_4$  and  $\text{CePO}_4$ , SSA of the catalysts containing 10 and 20% Ce would be 106 and 95  $\text{m}^2/\text{g}$ . The observed SSA values were smaller than those values suggesting that the catalysts were not

simple mixtures of the particles of individual phosphates.

It is very difficult to select a suitable temperature to compare the catalytic activity. Decomposition of  $\text{CCl}_2\text{F}_2$  over the  $\text{AlPO}_4$  catalysts has also been the case. The order of the activity is  $10\% > 5\% > 0\%$ , 20% in Ce concentration from the conversion curves. The reaction rates at  $400^\circ\text{C}$  is 33 times larger than that over  $\text{CePO}_4$ . On the contrary, the specific reaction rate ( $\mu\text{mole}/\text{m}^2$  per min) over  $\text{CePO}_4$  is 1.18 times larger than that over  $\text{AlPO}_4$ . Therefore, the results of the catalytic tests can be explained as follows. Decomposition of  $\text{CCl}_2\text{F}_2$  can proceed over both  $\text{AlPO}_4$  and  $\text{CePO}_4$  and the specific reaction rate over  $\text{CePO}_4$  is larger than that over  $\text{AlPO}_4$ . However, the increase in Ce concentration decreases the SSA of the catalysts, which is related to the activity. Consequently the  $\text{CCl}_2\text{F}_2$  conversion will take a maximum at 10 at.% Ce.

The  $\text{AlPO}_4$  catalyst calcined at  $1000^\circ\text{C}$  gives no diffraction peaks in XRD pattern but, Ce containing catalysts gave those due to  $\text{AlPO}_4$  and  $\text{CePO}_4$ . This reveals that there are two compounds,  $\text{AlPO}_4$  and  $\text{CePO}_4$ , in the catalysts.

The ionic sizes of  $\text{Al}^{3+}$ , 0.047 nm, and  $\text{Ce}^{3+}$ , 0.107 nm, are significantly different. The structure of  $\text{AlPO}_4$  is the same as that of  $\text{SiO}_2$  and the small  $\text{Al}^{3+}$  ions is surrounded by  $4\text{O}^{2-}$ . On the other hand,  $\text{CePO}_4$  has monazite structure and  $9\text{O}^{2-}$  coordinate to  $\text{Ce}^{3+}$  ion in monazite. Therefore, incorporation of Ce ions into  $\text{AlPO}_4$  matrix is thought to be difficult. However, the incorporation of  $\text{Al}^{3+}$  ions into matrix of  $\text{CePO}_4$  will be possible. The shift of the diffraction peaks can not be found but the formation of a small amount of  $\text{CePO}_4$  containing  $\text{Al}^{3+}$  at the grain boundary can not be ruled out. It is clear that a major part of the catalyst bulk is composed of  $\text{AlPO}_4$  and  $\text{CePO}_4$ , and the catalytic property will be depended on rather the surface structure than the bulk structure in these catalysts. Spectroscopic investigation is now in progress.

#### 3.4. Location and structure of Ce as a promoter element in the $\text{AlPO}_4$ catalysts

As shown in Section 3.3, the replacement of 10 mol% of  $\text{AlPO}_4$  by Ce brought about a

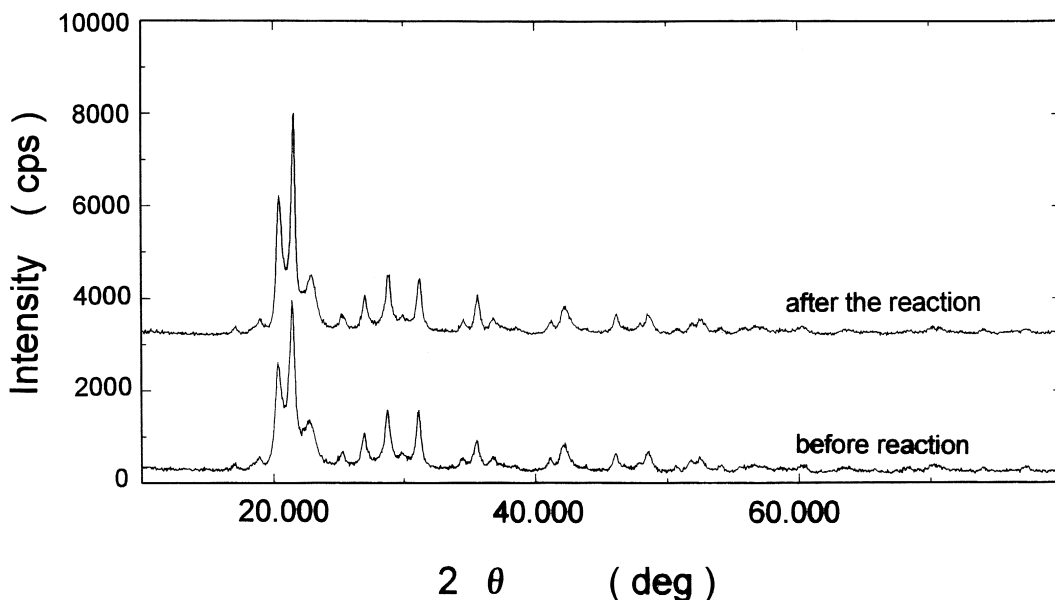


Fig. 5. XRD patterns of the  $\text{AlPO}_4$  catalyst promoted by 10 at.% of Ce. Reaction conditions of the catalytic test (90 h) are the same as given in Fig. 2.

significant increase in the catalytic activity for  $\text{CCl}_2\text{F}_2$  decomposition. Reaction temperature is lowered by about  $40^\circ\text{C}$  to obtain the same  $\text{CCl}_2\text{F}_2$  conversion. The promotion effect of Ce is quite clear. The XRD spectra of Ce promoted  $\text{AlPO}_4$  catalysts are shown in Fig. 5. Although the pure  $\text{AlPO}_4$  catalyst was amorphous after the calcination at  $1000^\circ\text{C}$  for 5 h, Ce promoted catalysts calcined at  $1000^\circ\text{C}$  for 5 h gave XRD peaks due to  $\text{AlPO}_4$  and  $\text{CePO}_4$  and the XRD pattern did not change after the catalytic test up  $500^\circ\text{C}$ . Crystallite sizes of  $\text{AlPO}_4$  and  $\text{CePO}_4$  were comparable, and were 13.0 and 16.9 nm, respectively. This promoted catalyst was prepared from an aqueous solution composed of 90% Al and 10% Ce nitrates and an aqueous solution containing stoichiometric amount of ortho-phosphoric acid. Chemical analysis revealed that the catalyst has almost the same concentration of  $\text{Al}^{3+}$ ,  $\text{Ce}^{3+}$ , and  $\text{PO}_4^{3-}$  as those of the parent liquor in preparation. In the catalyst preparation, the solution containing Al and Ce nitrates and phosphoric acid is strongly acidic and the pH of the solution is gradually increased by the addition of an aqueous solution containing ammonia. Since it is confirmed from separate experiments that  $\text{CePO}_4$  is precipitated at the lower pH than  $\text{AlPO}_4$ , there is possibility that  $\text{CePO}_4$  is precipitated at lower pH and then the mixture of  $\text{CePO}_4$  and  $\text{AlPO}_4$  is precipitated in the course of the addition of ammonia. If so, the surface concentration of Al will be higher than that of core of the precipitates. In order to examine the surface composition of the Ce promoted catalyst, the Ce (10%)– $\text{AlPO}_4$  catalyst calcined at  $1000^\circ\text{C}$ , was analyzed by means of XPS (Fig. 6). The mechanical mixture of separately prepared  $\text{AlPO}_4$  and  $\text{CePO}_4$  powders were used as reference samples. The pure  $\text{AlPO}_4$  and  $\text{CePO}_4$  gave characteristic signals at 75.5 and 886.4 eV which are assigned to the signals of Al (2P) and Ce (3d/5/2), respectively. Plotting the area ratio of these two signals against the Ce concentration of the reference catalysts with the composition of 1, 10 and 20 at.% of  $\text{CePO}_4$ , a straight line through the origin can be obtained.

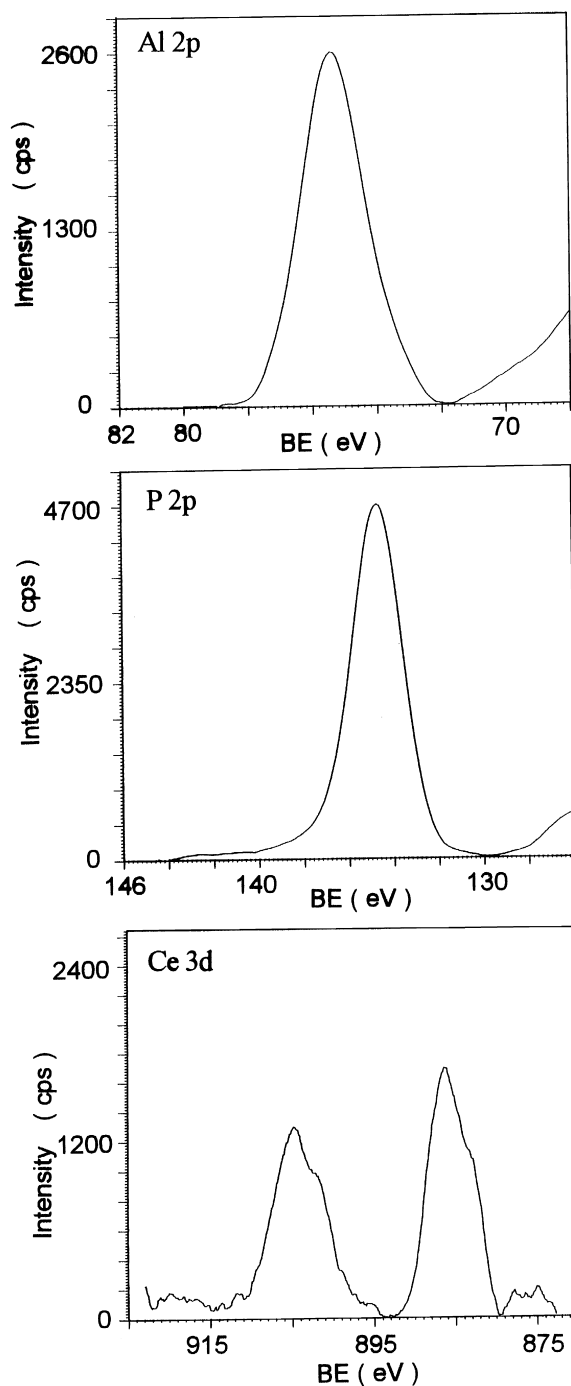


Fig. 6. XPS spectra of the  $\text{AlPO}_4$  catalyst promoted by 10 at.% of Ce.

Using this calibration line, the surface concentration of the catalyst which was prepared from

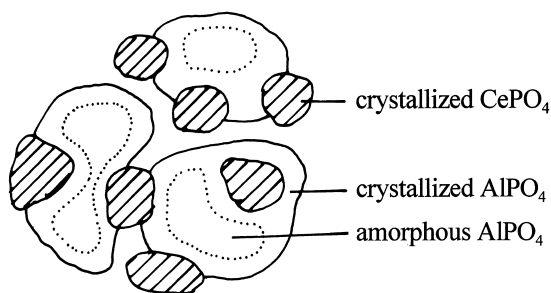


Fig. 7. Schematic plot of the structure of Ce-promoted  $\text{AlPO}_4$ .

an aqueous solution containing 90 mol% of Al and 10 mol% of Ce nitrates, was determined to 9.5 at.%. This value was closely near to that of the parent liquor in preparation, therefore it is concluded that the composition of the catalysts was uniform.

The SSA of  $\text{CePO}_4$  calcined at  $1000^\circ\text{C}$  was only  $3\text{ m}^2/\text{g}$  and it gave sharp diffraction peaks, suggesting that  $\text{CePO}_4$  is tend to crystallize. When the well ground mixture of powders of  $\text{CePO}_4$  and  $\text{AlPO}_4$  dried at  $200^\circ\text{C}$  was calcined at  $1000^\circ\text{C}$  for 5 h, as was expected, only small diffraction peaks due to  $\text{CePO}_4$  were observed. As mentioned before, in the case of the precipitate obtained from an aqueous solution containing 90 mol% of Al and 10 mol% of Ce nitrates, crystallization of  $\text{AlPO}_4$  and  $\text{CePO}_4$  took place by the calcination at the same temperature. The reason is as follows. In the case of the pure  $\text{AlPO}_4$ , extremely large network of  $\text{AlO}_4$  and  $\text{PO}_4$  units is extended and it resists to the crystallization of  $\text{AlPO}_4$  during calcination. On the other hand, mixed precipitate is constituted in such a way that amorphous  $\text{CePO}_4$  blocks are dispersed in the network of amorphous  $\text{AlPO}_4$ , and as the sintering of  $\text{CePO}_4$  is proceeded at higher temperatures, the crystallization of  $\text{AlPO}_4$  will take place at the boundary between  $\text{CePO}_4$  and  $\text{AlPO}_4$ . A sketch of the structure of Ce-promoted  $\text{AlPO}_4$  catalyst is given in Fig. 7. This hypothesis will later be checked by the adsorption of  $\text{NH}_3$  or water vapor, and Raman spectroscopy.

## 4. Conclusions

(1)  $\text{Al}(\text{PO}_3)_3$  is not an active species for the decomposition of  $\text{CCl}_2\text{F}_2$  and amorphous  $\text{AlPO}_4$  is thought to be an active species.

(2) Composition of the  $\text{AlPO}_4$  catalysts prepared at pH = 7.0 and 5.0 are Al:P = 52.8:47.2 and 50.5:49.5, respectively.  $\text{Al}_2\text{O}_3$  contained in the catalysts as impurity, gradually changes into  $\text{AlF}_3$  during the decomposition of  $\text{CCl}_2\text{F}_2$ , and this change bring about a slight decrease in the catalytic activity and promotes halogen exchanged reaction between  $\text{CCl}_2\text{F}_2$  and F to give  $\text{CClF}_3$ .

(3) Crystallization of  $\text{AlPO}_4$  does not take place in the presence of water vapor, but it takes place in the presence of both CFC and water vapor.

(4) Substitution of 5–10 mol% of Al ions in  $\text{AlPO}_4$  by Ce ions bring about a promotion effects in the  $\text{CCl}_2\text{F}_2$  decomposition. The optimum concentration of Ce is 10 at.%.

(5) The catalyst prepared by the co-precipitation method from solution containing Al and Ce nitrates and ortho-phosphoric acid and an aqueous solution of ammonia is composed of a mixture of fine  $\text{AlPO}_4$  and  $\text{CePO}_4$  particles, and surface and bulk compositions of the catalyst are almost the same.

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