Catalytic Decomposition of CF_4 over $AlPO_4$-Based Catalysts

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The most stable perfluorocarbon, CF_4, was decomposed to CO_2 at above 550 ℃ in the presence of water vapor over $AlPO_4$ in which 10 atomic % of Al ions are substituted by Ce. Catalytic activity slightly decreased within first 50 h and then took a stationary state for succeeding 50 h. No changes in the structure of catalyst were observed after 100 h reaction. Mg pyrophosphate and phosphates of Ca, B, Fe, Zn, Bi, and Ni were not active up to 700 ℃. The addition of Ce, La, Pr, Nd, Gd, Yb, Er, or Y into $AlPO_4$ increased the catalytic activity.

Chlorofluorocarbons (CFCs) including CCl_2F_2, CCl_2FCCF_2 had been widely utilized as a coolant of refregerator or cleaning agents in IC production. Roland and Molina[1] pointed out the possibility of the destruction of the ozone layer in the stratosphere, in 1974, and then some kinds of alternative HFCs such as CH_2FCF_3 and $CF_3CF_2CHCl_2$ have developed and actually utilized all over the world. Currently perfluorocarbons (PFC) such as CF_4, C_2F_6, and C_3F_8, have been utilized to etching and cleaning agents in IC production. However, PFCs show large green house effect which is several thousands of that of CO_2, for example, the green house potential of CF_4 is 6300 times larger than that of CO_2, and half-life of CF_4 is several hundreds years in ambient environment. So that it is of importance to destroy it after utilization and development of practical destruction method is strongly requested. But, it is very difficult to decompose under mild reaction conditions because these compounds have well stabilized C-F bonds. For example, the thermal decomposition of these materials requires the high temperatures of 1200-1400 ℃. Only the methods, which are chemically and economically eminent, will be utilized practically. Many decomposition methods have been proposed, so far.[2] Those are decomposition methods using (a) incineration, (b) cement kiln, (c) high frequency induced plasma, (d) UV, radioactive rays, or ultrasonic wave irradiation, (e) super critical water, and (f) catalysts. Method (a) has a disadvantage of dioxin formation. Method (b) is better way but the commercial cement has a limitation in halogen content, especially in Cl content, because it promotes corrosion of steel. Method (c) requires high running-costs. Methods (d) and (e) require complicated and pressure-resisting apparatus causing high costs, besides those are not so safe for workers.

Catalytic decomposition is thought to be the most simple, economical, and safe method. However, no studies concerning the catalytic decomposition of PFCs have reported. It is understandable that C-F bonds in PFC molecules are hard to decompose because those are well stabillized. Moreover, component of the catalysts will be reacted with formed hydrogen fluoride to make the corresponding fluorides, which have no catalytic activity for the decomposition, provided the decomposition of PFCs can be attained in the initial stage.

There is the same problem of the transformation of catalysts into fluorides in the decomposition of CFCs. Therefore, no catalysts which has long catalyst life are known irrespective of a large effort to explore active catalysts. Authors reported that CCl_2F_2 can be decomposed completely over the $AlPO_4$ based catalysts in the presence of water vapor at 350-450 ℃ and the catalysts were surprisingly resistant to hydrogen fluoride and were never transformed into fluoride therefore those have long catalyst life.[3-5] The essencial reaction is hydrolysis and CO_2 is sole product with carbon at a low CCl_2F_2 concentration of about 0.5 mole %. Currently authors found that these catalysts are effective for the decomposition of CF_4, which is the most stable molecule in PFCs, so that the application of $AlPO_4$-based catalysts for CF_4 decomposition will be reported in this paper.

The catalysts were prepared as following procedure. An aqueous solution of 0.25 M NH_3 was slowly added into an aqueous solution composed of metal nitrates and 85 wt% H_3PO_4 untill the pH of the solution reached to 4.5 with stiring and stand for overnight for aging. In preparation of Ce-promoted catalyst, 10 atomic% of $Al(NO_3)_3 9H_2O$ was substituted by $Ce(NO_3)_3 6H_2O$. The resulting precipitate was separeted by filteration and well washed with pure water. The obtained cake was dried at 120 ℃ for 10 h, and then pressed, sieved to 14-32 mesh and finally calcined at 1000 ℃ for 5 h. The $AlPO_4$ catalyst before reaction was amorphous and the $AlPO_4$ catalyst in which 10 atomic % of Al ions were substituted by Ce ions (denotes Ce10%-$AlPO_4$) gave small XRD diffraction peaks due to $AlPO_4$ and $CePO_4$.

The decomposition of CF_4 was carried out using an ordinary flow type reaction system with a 16-mm i.d. stainless steel tubular reactor. 9.0 g of a catalyst was packed into the reactor and a feed gas composed of 0.5 mol% CF_4, 55.3% water vapor, and the rest air, was introduced to the reactor at a rate of 70 cm^3/min. The gas eluted from the reactor was analyzed by GC equipped Polapak Q, Molecular sieves 5A, and Activated Alumina columns.

Catalytic activity of various metal phosphates for the decomposition of CF_4 was studied. Only $AlPO_4$ was effective for the decomposition of CF_4 and Mg pyrophosphate and phosphates of Ca, B, Fe, Zn, Bi, and Ni are not active up to 700 ℃. The results of the decomposition of CF_4 over the $AlPO_4$ based catalysts are shown in Figure 1. The experimental data was obtained at 3 h after reaching the desired temperature by sequential heating. CF_4 began to decompose at around 600 ℃ over the $AlPO_4$ catalyst and the 40% of CF_4 in the feed was converted at 700 ℃. The products were CO_2, HCl, and HF. No CO and any other halogenated carbon compounds were formed. The Ce10%-$AlPO_4$ catalyst was also highly effective for the decomposition of CF_4 and the reaction took place at around 550℃. This is the first example of the catalytic decomposition of CF_4.

The catalyst life is one of the most important facter for practical use, so that the change in the conversion of CF_4 was studied at 700 ℃ using the Ce10%-$AlPO_4$ catalyst. The results are shown in Figure 2. The initial conversion was about 74 %, which is slightly lower than the conversion appeared in Figure 1. This may be due to the difference of reaction conditions. The CF_4 conversion decreased with the time on stream for initial 40 h and then the conversion appeared to take the steady value of about

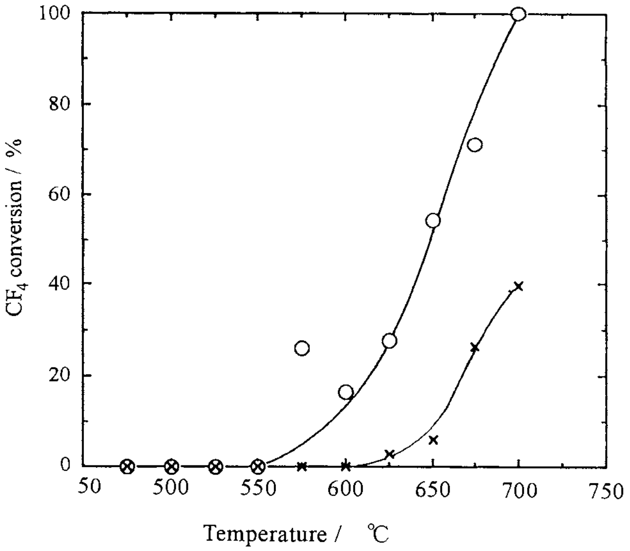

Figure 1. Decomposition of CF_4 over the $AlPO_4$ and Ce10%-$AlPO_4$ catalysts. Catalyst: 13.5 g; Feed (mol%): 0.51 CF_4, 8.8 O_2, 35.3 N_2, 55.4 H_2O, 94.3 cm^3/min. ○ Ce10%-$AlPO_4$, × $AlPO_4$.

52 %. The XRD patterns of the catalyst before and after the reaction for 100h are shown in Figure 3. As can be seen from the Figure 3, the catalyst before reaction is thought to be a mixture of $AlPO_4$ and $CePO_4$. No essencial change of the catalyst can be observed after the reaction for 100 h at high reaction temperature as 700 ℃. AlF_3 has the intrinsic diffraction peak at $2\theta = 14.9°$, but no peaks were observed in this region. It is noteworthy that the pure $AlPO_4$ is amorphous, therefore the addition of Ce as a promoter tends to crystallize the component phosphates. This resistance to fluorination may come from an intrinsic nature of the well-stabilized structure of $AlPO_4$.

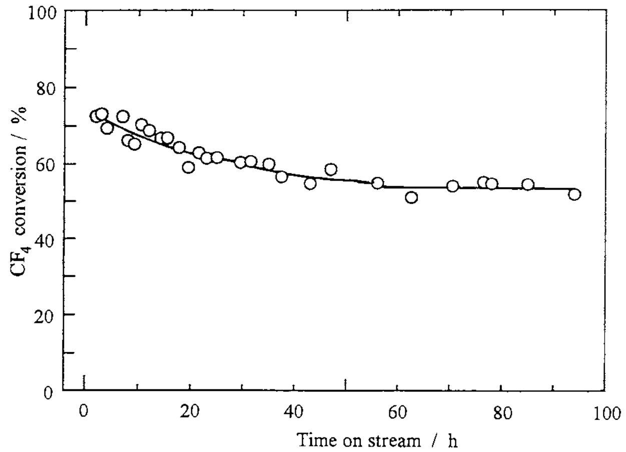

Figure 2. Effect of reaction time on the catalytic activity. Catalyst: Ce10%-$AlPO_4$, 9.30 g; Feed (mol%): 0.50 CF_4, 8.9 O_2, 35.1 N_2, 55.5 H_2O, 72.0 cm^3/min; 700 ℃.

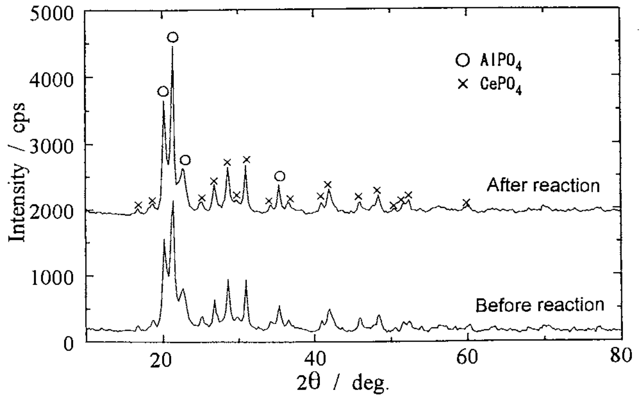

Figure 3. XRD patterns of the Ce10%-$AlPO_4$ catalyst before and after the CF_4 decomposition for 100 h at 700 ℃.

Table 1. The promotion effects of rare earth elements into $AlPO_4$ in the CF_4 decomposition.

Promoter[a]	Conversion /%	SSA /m^2g^{-1}
None ($AlPO_4$)	6.0	117
Ce	43.4	67
La	40.0	80
Pr	43.7	81
Nd	43.9	82
Gd	41.1	86
Yb	25.0	111
Er	19.1	69
Y	36.3	70

[a] 10 mole% of Al in $AlPO_4$ was substituted; 650℃; Reaction conditions are the same as those appeared in Figure 1.

The promotion effect of rare earth elements added into $AlPO_4$ was studied and the results at 650 ℃ are given in Table 1. The addition of rare earth elements brought about an increase in the catalytic activity. The addition of La, Pr, Nd, Gd, and Y promoted the activity to the comparable level with that of Ce-added catalyst, but the addition of Yb and Er, which belong to the group of heavy rare earth, gave less effects. It is concluded that rare earth elements are effective promoter to the $AlPO_4$ catalyst for CF_4 decomposition.

References and Notes

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