# Hydrolytic decomposition of PFCs over AlPO$_4$–Al$_2$O$_3$ catalyst†

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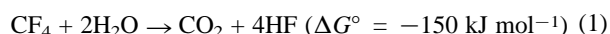
**AlPO$_4$–Al$_2$O$_3$ (Al/P > 9), prepared by impregnating (NH$_4$)$_2$HPO$_4$ on Boehmite, showed high catalytic activity and durability for the hydrolytic decomposition of perfluoro compounds even in the presence of water and HF.**

Perfluoro compounds (PFCs) such as CF$_4$, C$_2$F$_6$, C$_3$F$_8$, C$_4$F$_8$, NF$_3$, *etc.*, which are used as main cleaning and etching agents in the semiconductor process, are some representative greenhouse gases. They have extremely long atmospheric lifetimes and high global-warming potential (GWP). For example, CF$_4$, one representative of PFCs, has a lifetime of 50000 years and a GWP 6500 times higher than that of CO$_2$.[1–3] Therefore, the regulations for the PFCs have become more and more strict. Incineration and plasma have been considered as promising methods for the abatement of PFCs[4] but the high incineration temperature (> 1000 °C) and the lack of durability of plasma system and by-product formation have limited their commercial applications. Therefore, catalytic decomposition at low temperature has been suggested as a more practical alternative for the abatement of PFCs.[5–8]

As shown in equations (1) and (2), for the catalytic decomposition of PFCs, the hydrolysis by water is more effective than the oxidative decomposition by oxygen at temperatures below 750 °C.

$$CF_4 + 2H_2O \rightarrow CO_2 + 4HF \ (\Delta G° = -150 \text{ kJ mol}^{-1}) \ (1)$$

$$CF_4 + O_2 \rightarrow CO_2 + 2F_2 \ (\Delta G° = +494 \text{ kJ mol}^{-1}) \quad (2)$$

However, hydrolysis conditions are never benign to the catalyst because the catalyst always has to be exposed to the highly reactive HF and water at a temperature higher than 600 °C. Therefore, in the catalytic hydrolysis, it is most important to make a catalyst resistant to HF and water without loss of its catalytic activity.

In this study, it was found that AlPO$_4$–Al$_2$O$_3$ (Al/P > 9 mol/mol) was highly durable and effective for the catalytic decomposition of CF$_4$, C$_4$F$_8$ and NF$_3$ even in these severe reaction conditions. AlPO$_4$–Al$_2$O$_3$ was prepared simply by impregnating phosphate such as (NH$_4$)$_2$HPO$_4$ and H$_3$PO$_4$ on Boehmite (Catapal B, Condea Vista Co.), followed by drying at 100 °C for 5 h and calcining at 700 °C for 10 h. The hydrolysis of PFCs was carried out in a $\frac{3}{4}$ inch OD Inconel tube, and the products were analyzed with a GC equipped with a Porapak Q column.

Fig. 1 shows activity patterns of the AlPO$_4$–Al$_2$O$_3$ catalyst for hydrolytic decomposition of various types of PFCs such as CF$_4$, C$_4$F$_8$ and NF$_3$. The PFCs bearing nitrogen are less stable than those having carbon and could be decomposed at lower temperatures. For the decomposition of NF$_3$, 400 °C is enough but at least 650 °C is required for the complete decomposition of CF$_4$ and C$_4$F$_8$.

Selective hydrolysis is important in catalytic decomposition of PFCs because, if harmful by-products such as CO and NO*x* are formed, they have to be converted into safe compounds through a secondary treatment. Fortunately, during the hydroly-

sis of CF$_4$ over AlPO$_4$–Al$_2$O$_3$ at 700 °C, only CO$_2$ and HF were formed according to the equation (1) without any other by-product. To see how much the activity is influenced by the concentration of water and oxygen, CF$_4$ decomposition was carried out while changing their concentrations. As expected, decomposition activity was only influenced by the concentration of water without any effect by O$_2$; the activity decreased as the water concentration in the feed decreased and it showed almost zero activity in the absence of water. This means that the decomposition of CF$_4$ into CO$_2$ and HF occurred totally by hydrolysis.

In general, CF$_4$ exhausted in semiconductor processes does not exceed 5000 ppmv, which can be hydrolysed into CO$_2$ and HF without any by-product such as CO and NO*x* at temperatures lower than 700 °C (Fig. 1). To test the AlPO$_4$–Al$_2$O$_3$ catalyst in a more severe environment, the hydrolysis was carried out at 12000 ppmv of CF$_4$ and 750 °C. Shown in Fig. 2, the pure $\gamma$-alumina, although having a high initial hydrolysis activity, was easily deactivated. Only 40% conversion was obtained after 2 days of reaction due to the transformation of the $\gamma$-phase of alumina to a dense $\alpha$-phase by the HF produced in
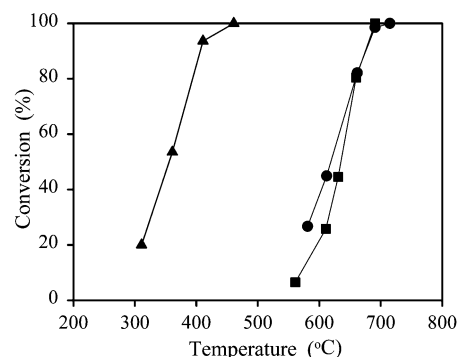


**Fig. 1** Conversions of CF$_4$ (●), C$_4$F$_8$ (■) and NF$_3$ (▲) over AlPO$_4$–Al$_2$O$_3$ (Al/P = 39) as a function of temperature (Catalyst = 5 g, PFCs = 1.1 ml min$^{-1}$, O$_2$ = 2.9 ml min$^{-1}$, He = 87 ml min$^{-1}$ and water = 0.04 ml min$^{-1}$, GHSV = 2 000 h$^{-1}$).
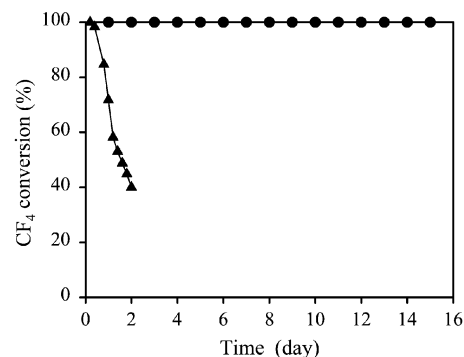


**Fig. 2** CF$_4$ conversions depending on time on stream over AlPO$_4$–Al$_2$O$_3$ (●, Al/P = 39) and $\gamma$-alumina (▲) ($T$ = 750 °C, catalyst = 5 g, PFCs = 1.1 ml min$^{-1}$, O$_2$ = 2.9 ml min$^{-1}$, He = 87 ml min$^{-1}$ and water = 0.04 ml min$^{-1}$, GHSV = 2 000 h$^{-1}$).

the reaction and water vapor, as will be mentioned later. However, the $AlPO_4$–$Al_2O_3$, $\gamma$-alumina modified with 2.5 mol% of phosphate, showed a big improvement in durability and 100% conversion of $CF_4$ was obtained without any deactivation even after 15 days of operation.

Previously, Hitachi Co. reported enhanced decomposition activity of $CF_4$ over the alumina catalyst modified with Zn or Ni, but the catalyst durability was not guaranteed.[9] $AlPO_4$–$Al_2O_3$ compares well and assures both activity and durability. This outstanding result was mainly caused by the phosphate added as a promoter to stabilize the $\gamma$-phase of alumina which is catalytically active for hydrolysis. In an atmospheric environment, the $\gamma$-phase of alumina is normally stable even at 800 °C without phase transformation into a more stable $\alpha$-phase. However, in the HF and water vapor environment it is transformed quickly into a dense $\alpha$-phase which is inactive catalytically. These phenomena could be seen clearly from the result of XRD and BET surface area of fresh and used catalysts (Fig. 3). In the case of pure $\gamma$-alumina, a considerable amount of $\alpha$-phase was formed with a big decrease in surface area within two days; surface area reduced from 198 to 6 $m^2 g^{-1}$ after the reaction. On the contrary, the $AlPO_4$–$Al_2O_3$ modified with phosphate showed negligible phase transformation and a relatively lower change in surface area from 132 to 81 $m^2 g^{-1}$ after 15 days of operation. In the catalytic dehydration of methanol over $AlPO_4$–$Al_2O_3$, Abbattista et al.[10] found that the phosphate prevented the transformation of $\gamma$-phase into $\alpha$-phase, which is in good agreement with our XRD result. The phosphate played an important role in protecting the $\gamma$-phase of alumina even in the presence of HF and water vapor. The phosphate existed as an amorphous phase because no XRD peaks corresponding to the crystalline $AlPO_4$ were observed.

The $AlPO_4$–$Al_2O_3$ catalysts having 6 different Al/P mol ratios of 8, 66, 56, 49, 39 and 24 were tested at 650 °C and initial conversions‡ of 82, 74, 71, 70, 69 and 48% $CF_4$ were obtained, respectively, The pure $\gamma$-alumina showed the highest activity and, as the content of P increased, the $CF_4$ conversion decreased monotonically. This means that only the $\gamma$-phase of alumina is effective for the hydrolysis and the added P just plays a role in stabilizing the $\gamma$-phase of alumina.

The change in the amount of acid site of fresh and used catalysts was monitored by the pyridine adsorption using an in situ FTIR cell, and then correlated with the decomposition activity. The fresh $\gamma$-alumina showed the largest number of Lewis acid sites while negligible acid sites were found over the used catalyst. In comparison with the $\gamma$-alumina, the $AlPO_4$–$Al_2O_3$(Al/P = 39) showed fewer Lewis acid sites but it still had considerable acid sites even after a long time of hydrolysis. This means that the hydrolysis activity is closely related with the
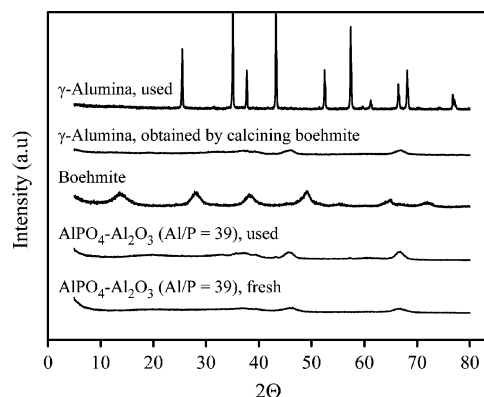
Lewis acid site of the catalyst as suggested in the previous results.[11–13]

Besides $\gamma$-alumina, many other solid oxides with acid sites could be used as a catalyst for hydrolysis. However, most of them are not resistant to the HF at high temperatures and are transformed into metal fluoride or oxyfluoride which is volatile and catalytically inactive. In CFCs decomposition, the oxide catalysts also suffered from the phase transformation into fluoride.[11,12,15] Therefore, the catalysts were modified so as to avoid the formation of fluoride which is inactive for hydrolysis. Fortunately, according to the results of XRD and energy dispersive X-ray analysis, no such fluoride compound was detected in the $AlPO_4$–$Al_2O_3$ even after a long exposure to the reaction. The absence of fluoride accumulation could be explained by the enhanced reverse reaction of equation (3) due

$$Al_2O_3 + 6HF \leftrightarrow 2AlF_3 + 3H_2O \qquad (3)$$
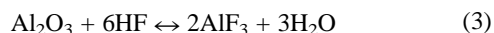
to the excess $H_2O$ present in the reactant. Myasnikov and Bogachev[16] have reported that the activation energy of the reverse reaction of equation (3) is 89 $kJ mol^{-1}$ and its rate is proportional to $\frac{3}{2}$ order of partial pressure of water.

In summary, $CF_4$ could be decomposed effectively into $CO_2$ and HF without by-products through hydrolysis over $\gamma$-alumina that has Lewis acid sites. However, due to the lack of phase stability, modification with a promoter is required. The impregnation of phosphate provided one of the most efficient ways for stabilising the $\gamma$-phase of alumina and its catalytic activity was maintained for more than 15 days without deactivation even in the presence of HF. The biggest advantage of the $AlPO_4$–$Al_2O_3$ catalyst is that it can be prepared conveniently and cheaply. We are now carrying out a large-scale durability test to expand its potential as a commercial PFCs abatement.

## Notes and references

‡ This conversion was measured after 1 hour of the reaction.

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**Fig. 3** XRD patterns of $\gamma$-alumina and $AlPO_4$–$Al_2O_3$ before and after the hydrolysis of $CF_4$ at 750 °C for 45 hours.