A Strategy to Protect Al_2O_3-based PFC Decomposition Catalyst from Deactivation

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γ-Al_2O_3 is one of the most active catalysts for hydrolytic decomposition of PFCs but it has been suffered from deactivation. The main reason for the deactivation was the transformation of catalytically active γ-phase into an inactive α-phase by the HF produced during the decomposition of PFCs. To prohibit the phase transformation, structure modifiers such as $ZnAl_2O_4$ and $AlPO_4$ were strongly required, which resulted in a remarkable catalyst durability.

Perfluorocompounds (PFCs) such as CF_4, C_2F_6, C_3F_8, SF_6, and NF_3 are used extensively as etching or cleaning gases in semiconductor or LCD processes. Because they are quite stable a temperature higher than 1000 °C is required for their thermal decomposition. Also, because of their high global warming potential (GWP) and long life time,[1,2] their regulations become more and more strict and several types of abatement technologies such as direct/indirect incineration, plasma decomposition, and catalytic decomposition have been suggested. Among the suggested ones, catalytic decomposition has been regarded as the most promising one. However, because of the lack of catalyst durability its commercialization has been delayed.[3–7] That is, γ-Al_2O_3 is known to be a most active catalyst for hydrolytic decomposition of PFCs but it has been suffered from rapid deactivation.[8,9]

The main reason for the deactivation is thought to be the transformation of catalytically active γ-Al_2O_3 into inactive ones such as AlF_3 and α-Al_2O_3 by the HF produced in PFC decomposition process through the reaction of 1 → 2 → 3.[10]

$$CF_4 + 2H_2O \rightarrow CO_2 + 4HF \qquad (1)$$

$$\gamma\text{-}Al_2O_3 + 6HF \rightarrow 2AlF_3 + 3H_2O \qquad (2)$$

$$2AlF_3 + 3H_2O \rightarrow \alpha\text{-}Al_2O_3 + 6HF \qquad (3)$$

Recently, we found that the stabilities of γ-Al_2O_3 catalyst could be improved remarkably by the introduction of small amount of P or Zn as a structure modifier.[11] Therefore, in this paper, we tried to elucidate deactivation mode of γ-Al_2O_3 catalyst and suggest a strategy to prevent its deactivation.

Three types of catalysts were prepared and their catalytic activities were tested in a fixed bed reactor while flowing 7000-ppm CF_4 and 34.5% water vapor at GHSV of 2000 h^{-1}; (i) a bare γ-Al_2O_3 by calcining a boehmite (Condea Vista Co.) at 700 °C for 10 h and two modified ones by impregnating (ii) 10 mol % of $Zn(NO_3)_2$ (10% Zn/Al_2O_3) and (iii) 6 mol % of H_3PO_4 (6% $AlPO_4/Al_2O_3$) on γ-Al_2O_3. Initially all of the prepared catalysts revealed 100% CF_4 conversion but they revealed quite different time dependence (Figure 1).While the unmodified γ-Al_2O_3 deactivated rapidly within 15 h, no deactivations were observed over the 10% Zn/Al_2O_3 up to 50 h and over the 6% $AlPO_4/Al_2O_3$ even after 200 h.

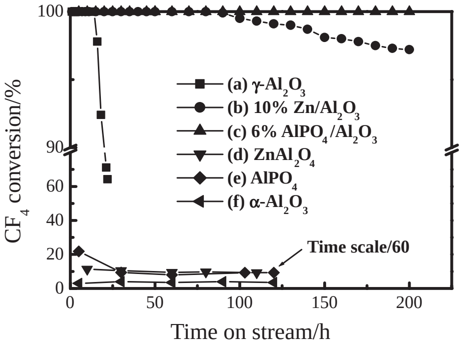


Figure 1. CF_4 conversion over (a) γ-Al_2O_3, (b) 10% Zn/Al_2O_3, (c) 6% $AlPO_4/Al_2O_3$, (d) $ZnAl_2O_4$, (e) $AlPO_4$, and (f) α-Al_2O_3 (reaction condition: 7000-ppm CF_4 and 34.5% H_2O in He balance, $T = 750$ °C, GHSV $= 2000\,h^{-1}$).

To investigate how the catalysts were influenced by the HF produced in decomposition process, the γ-Al_2O_3 and 10% Zn/Al_2O_3 were exposed to the HF and H_2O at 300–750 °C for 25 h and then characterized by XRD, BET and SEM.

As shown in Figures 2 and 3, the bare γ-Al_2O_3 and modified one (10% Zn/Al_2O_3) revealed big change in structure and morphology depending on the exposure temperature of HF. At 300 °C, considerable amount of AlF_3 was formed without change in morphology through the reaction 2 (Figures 2b, 3a-1, and 3b-1). However, at the temperatures higher than 400 °C the γ-Al_2O_3 and the modified 10% Zn/Al_2O_3 revealed complete different structures and morphologies. That is, the bare γ-Al_2O_3 was transformed to a crystalline AlF_3 at 500 °C and finally changed to a dense α-Al_2O_3 at 750 °C. However, different from the bare γ-Al_2O_3 spinel $ZnAl_2O_4$ phase was observed over the 10% Zn/Al_2O_3 at 750 °C with small amount of α-Al_2O_3. This result clearly indicates that the phase transformation suggested in Eq 4 is prohibited on the 10% Zn/Al_2O_3 by the formation of $ZnAl_2O_4$ resistant to the HF.

$$\gamma\text{-}Al_2O_3 + 6HF \rightarrow 2AlF_3 + 3H_2O \rightarrow \alpha\text{-}Al_2O_3 + 6HF \qquad (4)$$

Also, the effect of Zn as a structure modifier could be seen clearly in the SEM analysis. When the irregular shaped porous γ-Al_2O_3 was exposed to the HF at 750 °C, it transformed to a disk-like crystalline α-phase. However, no change in morphology was observed over the 10% Zn/Al_2O_3 modified with Zn (Figures 3a-2 and 3b-2). Considering that the phase transformation of γ-Al_2O_3 into α-Al_2O_3 does not take place below 800 °C in conventional air atmosphere, it also could be speculated that the transformation of γ-Al_2O_3 to α-Al_2O_3 was mainly caused by the HF through the reaction 4.

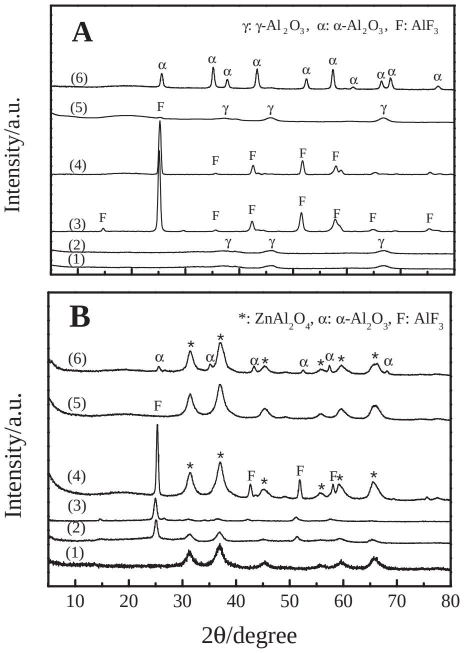
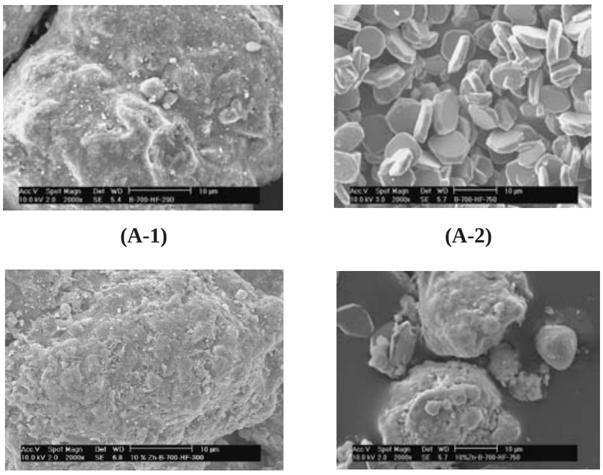


Figure 2. XRD patterns of (A) γ-Al_2O_3 and (B) 10% Zn/Al_2O_3 exposed to HF and H_2O at different temperatures: (1) fresh catalysts, (2) 300, (3) 400, (4) 500, (5) 600, (6) 750 °C.


(A-1) (A-2)

(B-1) (B-2)

Figure 3. SEM images of (A) pure γ-Al_2O_3 and (B) 10% Zn/Al_2O_3 exposed to HF and H_2O at (1) 300 and (2) 750 °C for 25 h.

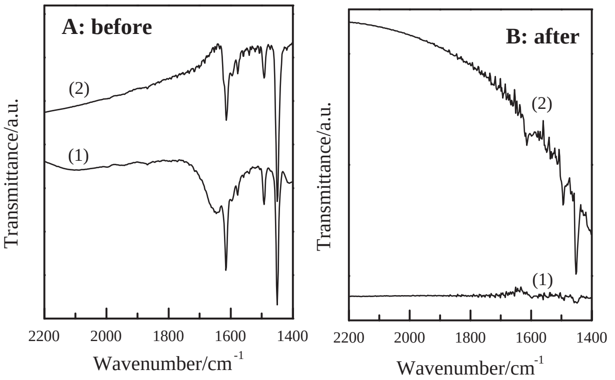


Figure 4. FT-IR spectra of (1) γ-Al_2O_3 and (2) 10% Zn/Al_2O_3 after pyridine adsorption: (A) before and (B) after hydrolytic decomposition of CF_4 at 750 °C for 24 h.

The γ-Al_2O_3 and 10% Zn/Al_2O_3 also showed difference in acidity after being exposed to the HF at high temperature. The acidities of catalysts before and after CF_4 decomposition reaction was compared using in situ FT-IR cell after pyridine adsorption (Figure 4). Both of the fresh γ-Al_2O_3 and 10% Zn/Al_2O_3 catalysts revealed strong Lewis acidity having peaks at 1450, 1577, and 1611 cm^{-1} by the coordinatively adsorbed pyridine without any Brønsted acidity.[12,13] However, most of the acid sites on the γ-Al_2O_3 disappeared after reaction for 24 h but considerable amount of acid sites still existed on the 10% Zn/Al_2O_3. This result means that the Lewis acid sites are closely related to the decomposition activity of PFCs and the Zn played an important role to prohibit the phase transformation γ-Al_2O_3 into α-Al_2O_3.

Even though the Zn is an effective modifier to reduce the deactivation of γ-Al_2O_3 catalysts, the 10% Zn/Al_2O_3 catalyst deactivated gradually as the reaction proceeded. According to our recent result, aluminum phosphate was a more efficient modifier than the Zn to protect deactivation of γ-Al_2O_3-based catalyst (Figure 1(c), refer to the Ref. 11 for more details).

In conclusion, for the development of durable γ-Al_2O_3-based catalyst for the hydrolytic decomposition of PFCs it is very important to find an effective structure modifier to protect catalytically active γ-Al_2O_3 from the phase transformation at high temperature and HF environment.

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