The modification and stability of γ-Al$_2$O$_3$ based catalysts for hydrolytic decomposition of CF$_4$

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Abstract

Al$_2$O$_3$ of different phases were applied in the hydrolytic decomposition of CF$_4$ with water into CO$_2$ and HF at 750 °C. It was found that γ-Al$_2$O$_3$ was an active catalytic phase, but it deactivated rapidly due to the transformation into a catalytically inactive α-Al$_2$O$_3$ affected by the HF produced in the reaction. To increase catalytic stability, the γ-Al$_2$O$_3$ was modified with various types of metals such as Zn, Ni, Mg, Sr and Ba. When the γ-Al$_2$O$_3$ was modified with Zn and Ni, the catalytic stability was enhanced remarkably, which was mainly due to the formation of Zn or Ni aluminates resistant to the HF on catalyst surface during the reaction. Mg, Sr and Ba were also good structural stabilizers for γ-Al$_2$O$_3$, but the catalytic activity for the CF$_4$ decomposition decreased due to their neutralizing effect on acid sites of γ-Al$_2$O$_3$. The FTIR spectra of adsorbed pyridine revealed that Lewis acidity of γ-Al$_2$O$_3$ based catalysts played an important role and the efficient structure modifier can preserve the Lewis acid sites on the catalysts in the CF$_4$ hydrolysis process.
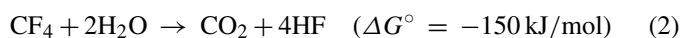© 2006 Elsevier B.V. All rights reserved.

Keywords: Hydrolytic decomposition of CF$_4$; γ-Al$_2$O$_3$; Structure modifiers; Catalyst stability; Lewis acidity

1. Introduction

Perfluorocompounds (PFCs), such as CF$_4$, NF$_3$ and SF$_6$ have been widely used as etching and cleaning agents in semiconductor processes. The PFCs have high global warming potential (GWP) and long lifetime; for example, CF$_4$ has a GWP 6500 relative to that of CO$_2$ and a lifetime of 50,000 years [1,2]. Therefore, it is strongly required to destruct the exhausted PFCs, which are included in the Kyoto Protocol. Several technologies of PFCs abatement, such as incineration, plasma and catalytic decomposition have been suggested. Among them the plasma decomposition has ever been considered as one of the most probable candidates; however, due to the lack of plasma stability and the formation of by-products, such as NO$_x$, the interest in it has decreased and new abatement technologies have been searched for. Recently, the catalytic decomposition has been suggested as

a more practical and economical method for the abatement of PFCs.

As can be seen in Eqs. (1) and (2), the water reveals high thermodynamically negative Gibbs free energy and is effective in the PFCs decomposition:

$$CF_4 + O_2 \rightarrow CO_2 + 2F_2 \quad (\Delta G^\circ = 494 \, kJ/mol) \tag{1}$$

$$CF_4 + 2H_2O \rightarrow CO_2 + 4HF \quad (\Delta G^\circ = -150 \, kJ/mol) \tag{2}$$

In the hydrolytic decomposition of PFCs, highly reactive and corrosive HF is produced together with CO$_2$. According to Farris et al. [3], the HF produced in the hydrolytic decomposition of C$_3$F$_6$ over Pt/Al$_2$O$_3$ led to a rapid deactivation of the catalyst due to the formation of AlF$_3$ through the interaction of Al$_2$O$_3$ with the produced HF. It was reported that in CF$_4$ hydrolytic decomposition over the AlPO$_4$ catalyst at 700 °C, the conversion of CF$_4$ was reduced from 74% at the initial stage to 52% after 95 h of time on stream [4,5].

According to our recent results [6,7], the influence of HF on γ-Al$_2$O$_3$ catalyst was strongly dependent on the reaction

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temperature. When γ-Al_2O_3 was used as a catalyst in CF_4 hydrolytic decomposition under excess water, it can be transformed into AlF_3 or α-Al_2O_3 depending on reaction temperature. That is, when γ-Al_2O_3 was exposed to the environment of CF_4 hydrolysis below 600 °C AlF_3 phase was observed predominantly on the catalyst, but α-Al_2O_3 appeared above 600 °C. Consequently, we made a conclusion that the transformation of γ-Al_2O_3 into AlF_3 or α-Al_2O_3 affected by HF was responsible for the deactivation of γ-Al_2O_3 based catalysts. Therefore, it is very important to prepare a catalyst resistant to the produced HF without deactivation in the catalytic decomposition of PFCs.

Recently, some patents claimed that a long lifetime and high activity for PFCs catalytic decomposition could be guaranteed over modified γ-Al_2O_3 [8–15]. Previous results reported that the stability of γ-Al_2O_3 catalysts for the CF_4 decomposition could be improved remarkably by the introduction of some other metals, such as zinc and nickel as a structure modifier [16,17]. They explained that the introduced metals converted into metal aluminates during calcination, which brought increased Lewis acidity and made the catalyst more resistant to HF. However, the reason for the deactivation was not explained well.

Recently, it was found that the deactivation of γ-Al_2O_3 strongly depended on the reaction temperature and was mainly caused by the phase transformation of catalysts. At the reaction temperature lower than 680 °C, no severe phase transformation of catalysts was observed [16,17]. However, if the reaction temperature was higher than 700 °C, where 100% of CF_4 conversion was attained, the phase transformation of γ-Al_2O_3 into α-Al_2O_3 occurred severely even over Ni and Zn modified alumina catalysts.

Therefore, in the present study, we investigated phase transformation behavior of modified alumina catalyst at high reaction temperature and tried to correlate the deactivation rate with the loadings of metal modifiers. Different types of aluminum phases were formed on the γ-Al_2O_3 by calcining the γ-Al_2O_3 after modifying with different types of metal precursors such as Zn, Ni, Mg, Sr and Ba. Then the physicochemical properties of the catalysts were investigated by BET surface area measurement, XRD, SEM, and FTIR of pyridine adsorption and correlated with their catalytic activity and stability.

2. Experimental

2.1. Catalyst preparation

For hydrolytic decomposition of CF_4, four types of alumina precursors, an alumina of mixed phases from Strem Chemicals Co., boehmite from Condea Chemical Co., amorphous $Al(OH)_3$ from Aldrich Chemical Co. and gibbsite from Zeotech Korea Co. were used after calcination at 700 °C in air for 10 h.

For the modification of γ-Al_2O_3, the boehmite was incipiently impregnated with $Zn(NO_3)_2 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Sr(NO_3)_2$ or $Ba(NO_3)_2$ solution for 24 h, and followed by drying at 100 °C and calcining at 700 °C for 10 h. The prepared catalysts were denoted by x% M/Al_2O_3, where M and x indicates the metal element and its atomic percentage in M/(M + Al), respectively.

2.2. Catalytic reaction

The hydrolytic decomposition of CF_4 was carried out in a continuous fixed-bed 3/4 in. inconel reactor at 750 °C under atmospheric pressure with flowing 0.7% CF_4, 34.5% H_2O and balanced He at a gas hourly space velocity (GHSV) of 2000 h^{-1}. A syringe pump was used to constantly introduce the required amount of water. The effluent gas was washed by distilled water to remove the produced HF and passed through a cold trap to remove the water, and then analyzed with a HP5890 GC equipped with a Porapak Q column (Ø0.3 cm × 2 m, column temperature 40 °C) and a TCD detector.

2.3. Catalyst characterization

For the characterization of physicochemical properties of the bare and modified γ-Al_2O_3 catalysts, BET surface area measurement, SEM, XRD and FTIR of adsorbed pyridine were applied.

BET surface area measurements were performed using an automated nitrogen adsorption apparatus (ASAP2400, Micromeritics). Prior to the measurements, the samples were degassed at 300 °C for 3 h.

The crystallographic phases of catalysts were examined by a Rigaku D-max IIIB X-ray diffractometer with Ni filtered Cu Kα radiation.
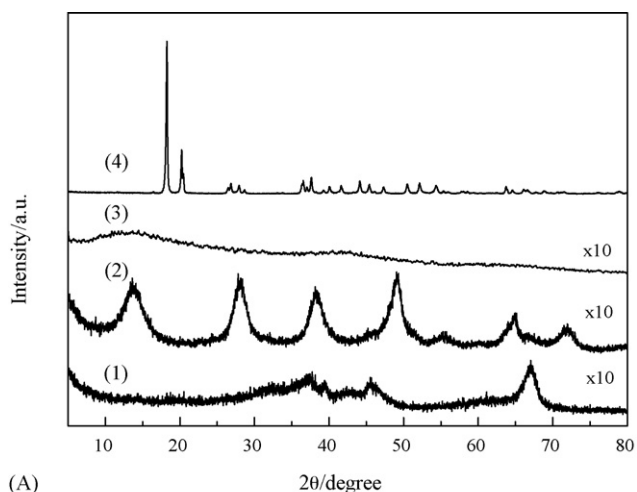
SEM-EDX analysis was done using a JEOL JSM-840A scanning electron microscope equipped with an energy dispersive X-ray detector.

Surface acidity of catalysts was measured with a Nicolet Avatar360 FTIR spectrometer after pyridine adsorption. A self-supported sample was prepared by pressing and then treated under vacuum at 300 °C for 3 h in an in situ IR cell. After cooling to room temperature, the pretreated samples were exposed to pyridine vapor, and then evacuated for 1 h at 100, 200, 300 and 400 °C, respectively. After the treatment, the IR spectra were obtained at ambient temperature.
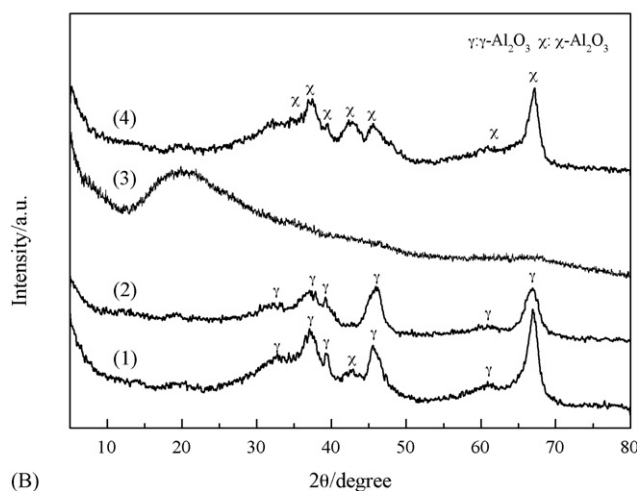
3. Results and discussion

3.1. Catalytic activity of alumina of different phases

For the preparation of aluminas of different phases, four kinds of alumina precursors having the original structure of boehmite (AlOOH), an alumina with mixed phases, amorphous $Al(OH)_3$, gibbsite were used, respectively. Fig. 1 shows the XRD patterns of these alumina precursors as purchased and calcined at 700 °C for 10 h in air. In XRD patterns, the χ-Al_2O_3 shows characteristic peaks at 2θ value of 42.8°, 44.4° and 67.3° with relative intensities of 40, 11 and 100 (PDF no. 34–493), while γ-Al_2O_3 has peaks at 31.9°, 45.8° and 66.7° with relative intensities of 45, 80 and 100 (PDF no. 29–63), respectively. So, the χ- and γ-Al_2O_3 phases can be distinguished by the presence of XRD peaks at 42.8° and 31.9°. As shown in Fig. 1, four alumina precursors as purchased showed the XRD patterns of a χ- and γ-Al_2O_3 mixture, boehmite (AlOOH), gibbsite and amorphous $Al(OH)_3$, respectively. However, after calcination at 700 °C in air, they were transformed into different types of alu-

Fig. 2. Hydrolytic conversion of CF_4 at 750 °C over aluminas obtained by calcining different precursors.

Fig. 1. XRD patterns of (1) Al_2O_3 of mixed phases, (2) boehmite, (3) amorphous $Al(OH)_3$, (4) gibbsite (A) as received and (B) after calcinations at 700 °C for 10 h in air.

mina. When the boehmite was calcined the pure γ-Al_2O_3 phase was obtained, while a mixture of χ- and γ-Al_2O_3, amorphous Al_2O_3 and χ-Al_2O_3 were obtained from the Al_2O_3 of mixed phases, amorphous $Al(OH)_3$ and gibbsite, respectively.

As shown in Fig. 2, the decomposition of CF_4 was strongly influenced by the types of alumina phase. The γ-Al_2O_3 obtained by calcining boehmite revealed the highest activity during the initial stage; 100% conversion of CF_4 was obtained at the beginning of reaction. However, different from γ-Al_2O_3, the other three types of alumina showed quite low activity and only less than 30% CF_4 conversion was obtained. These results clearly reveal that of all the aluminas of various types, only the one with γ-phase is catalytically effective for the hydrolytic decomposition of CF_4.

To find the reasons for the high catalytic activity of γ-Al_2O_3, the physicochemical properties such as BET surface area and morphology of the four types of alumina were investigated and compared.

The surface area of Al_2O_3 with mixed phases, boehmite AlOOH, gibbsite $Al(OH)_3$ and amorphous $Al(OH)_3$ was 179.3, 330.3, 286.3 and 37.4 $m^2\,g^{-1}$ as received and was changed to

139.5, 197.9, 168.3 and 51.7 $m^2\,g^{-1}$ after calcination at 700 °C, respectively. Among them, the boehmite showed the highest surface area, which was maintained after calcination even though its absolute value was reduced. The Al_2O_3 of mixed phases or χ-Al_2O_3 from gibbsite also revealed relatively high surface area, which was higher than 130 $m^2\,g^{-1}$ even after calcination at 700 °C. Generally, the surface area decreases after the calcination, but in the case of amorphous $Al(OH)_3$, its surface area increased after calcination at 700 °C. The result reveals all of the aluminas have surface area higher than 50 $m^2\,g^{-1}$; however, their catalytic activity for CF_4 decomposition was quite low except for the γ-Al_2O_3 obtained from boehmite, which infers that the large difference in activity of different phases of alumina did not result from the difference in their surface area.

The morphology of these aluminas was monitored by SEM and shown in Fig. 3. The Al_2O_3 of mixed phases and γ-Al_2O_3 from boehmite have a granule size larger than 20 and 8 μm, respectively, while the χ-Al_2O_3 from gibbsite and amorphous Al_2O_3 consisted of fine granules having particle size less than 1 μm. The size of granules was in the following order: Al_2O_3 with mixed χ- and γ-phases > γ-Al_2O_3 > χ-Al_2O_3 > amorphous Al_2O_3, which has no correlation with their catalytic activity for the CF_4 decomposition.

The results of XRD, BET and SEM reveal that the decomposition conversion of CF_4 depends more strongly on the chemical properties of Al_2O_3 catalysts than the physical ones. Only the γ-Al_2O_3 was effective for the hydrolytic decomposition of CF_4, but when the γ-Al_2O_3 was exposed to the reaction conditions for 22 h, it was transformed into a dense α-Al_2O_3 [7], which led to rapid deactivation and a short lifetime of catalyst. Considering that the γ-Al_2O_3 is stable and the transformation of γ-Al_2O_3 into α-Al_2O_3 does not take place in air at 750 °C, it is inferred that the formation of α-Al_2O_3 in the CF_4 hydrolysis mainly resulted from the produced HF.

In summary, γ-Al_2O_3 is an effective phase for the CF_4 hydrolytic decomposition but it itself is not stable enough to resist the produced HF and further modification is strongly required to stabilize the catalytically active γ-phase.
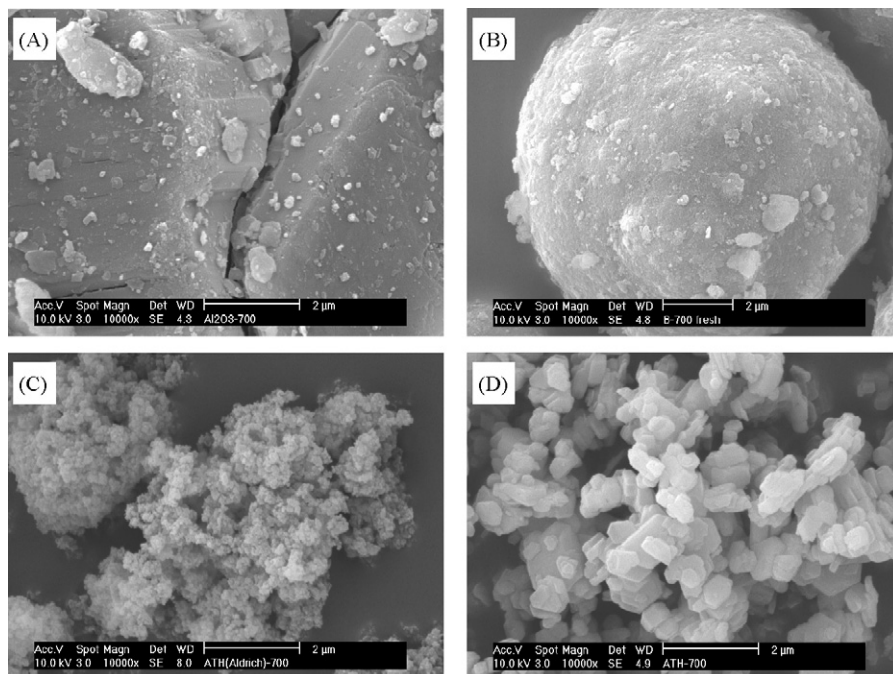
Fig. 3. SEM images of (A) Al_2O_3 of mixed phases, (B) boehmite, (C) amorphous $Al(OH)_3$ and (D) gibbsite after calcinations at 700 °C for 10 h in air (magnification: 10,000×).

3.2. Catalytic activity of modified γ-Al₂O₃

To improve the stability of γ-Al_2O_3, it was modified with Zn, Ni, Mg, Sr or Ba oxide and the activity of modified γ-Al_2O_3 catalysts was tested for CF_4 hydrolytic decomposition.

Fig. 4(A) shows the CF_4 conversion depending on reaction time over the bare and Zn modified γ-Al_2O_3 (Zn/Al_2O_3) catalysts. Initially all of the catalysts revealed 100% CF_4 conversion, but they showed quite different dependence upon time on stream. The bare γ-Al_2O_3 deactivated rapidly within 15 h; however, the Zn/Al_2O_3 catalysts showed significant enhancement of stability and no loss in activity was found for the one with 20% Zn loading throughout 70 h of time on stream. As shown in Fig. 4(B), the γ-Al_2O_3 modified with Ni was quite similar to Zn/Al_2O_3 but the effect of Ni was not so high as that of Zn. That is, the addition of Ni to the γ-Al_2O_3 also brought about an improvement in catalytic stability, but the activity of the Ni-modified Al_2O_3 for the CF_4 decomposition was less than that of Zn/Al_2O_3.

The XRD peaks in Fig. 5(A) indicates zinc nitrate loaded on the γ-Al_2O_3 surface decomposed and reacted with γ-Al_2O_3 to form $ZnAl_2O_4$ in the calcination process. The higher the loading of Zn, the more $ZnAl_2O_4$ was formed on the prepared catalysts surface, which prevented the formation of the catalytically inactive α-Al_2O_3 phase on the Zn/Al_2O_3 catalysts during the CF_4 decomposition reaction (Fig. 5(B)). As listed in Table 1, when γ-Al_2O_3 was modified with Zn, a decrease in surface area was observed in their fresh state, that is γ-Al_2O_3 > 5% Zn/Al_2O_3 > 20% Zn/Al_2O_3. However, a reverse trend was observed over the spent catalysts; the surface area of the catalysts after the CF_4 decomposition and the used/fresh value increased in the order of bare Al_2O_3 < 5% Zn/Al_2O_3 < 20% Zn/Al_2O_3.
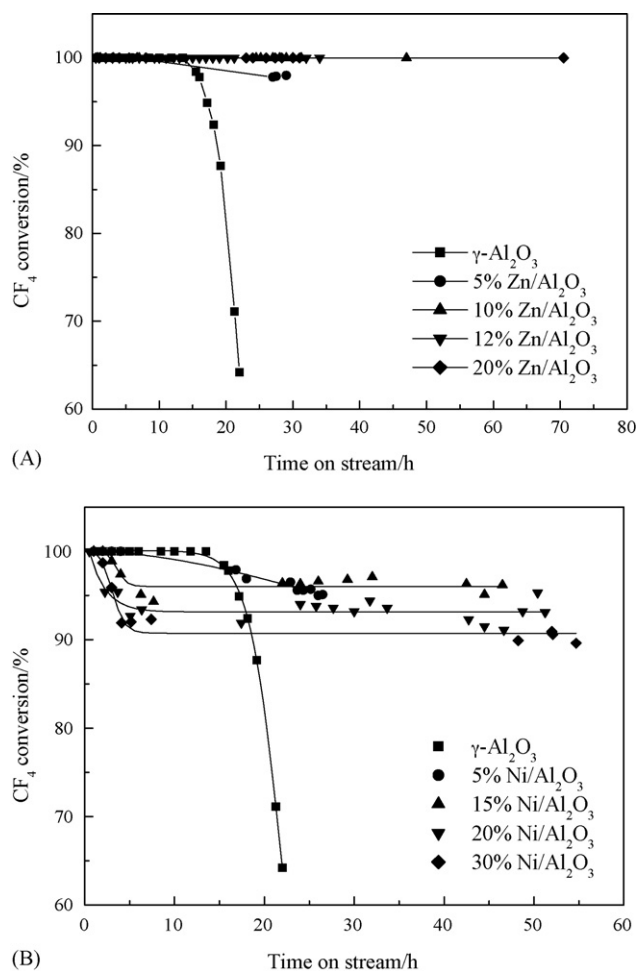

Fig. 4. CF_4 hydrolytic conversion over (A) Zn/Al_2O_3 and (B) Ni/Al_2O_3 catalysts.
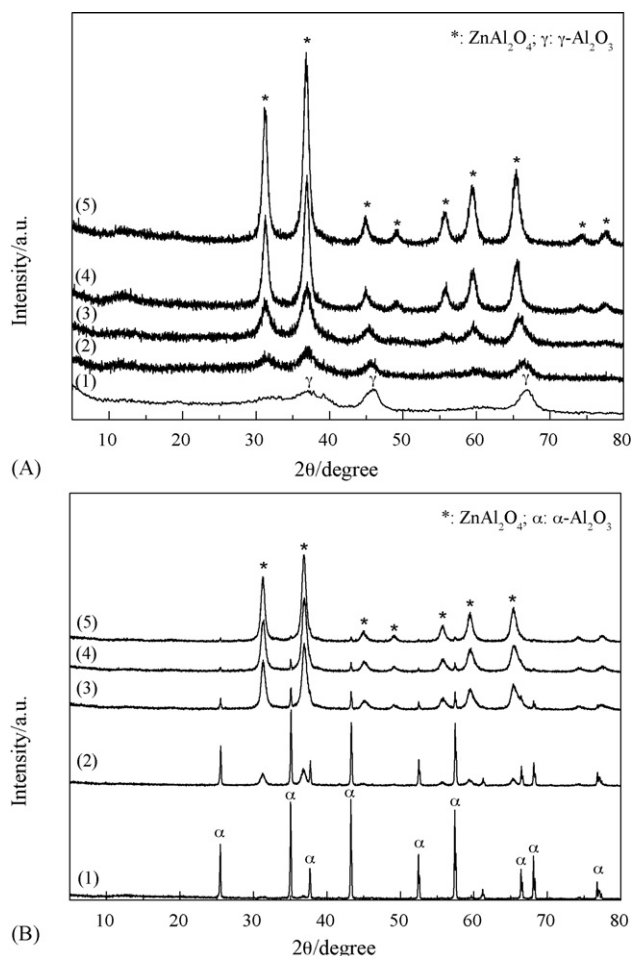
Fig. 5. XRD patterns of (A) fresh and (B) used Zn/Al$_2$O$_3$ with Zn mole percentage of (1) 0%, (2) 5%, (3) 10%, (4) 12% and (5) 20% (for the used catalysts, the reaction time could be seen from Fig. 4(A)).
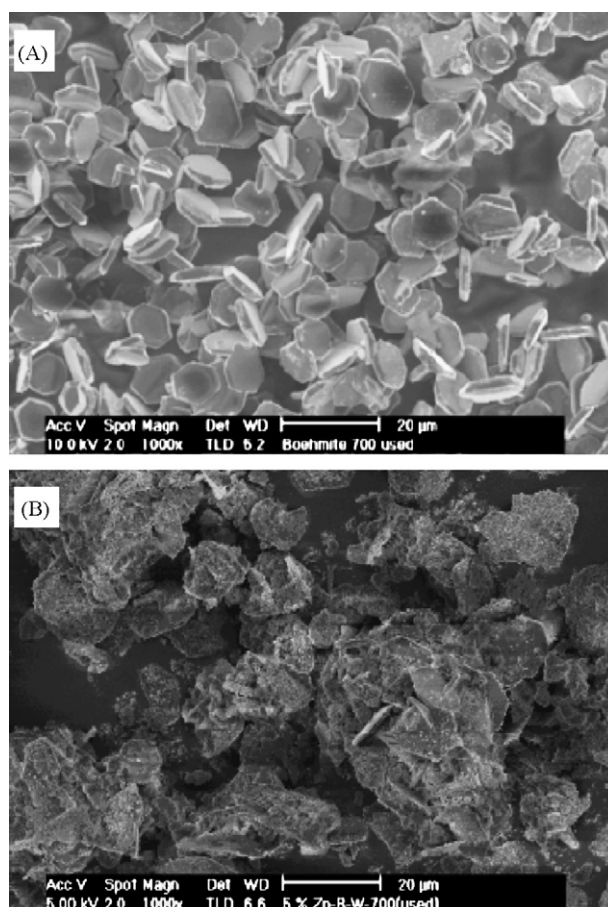
Fig. 6. SEM images of (A) γ-Al$_2$O$_3$ and (B) 5% Zn/Al$_2$O$_3$ catalysts after CF$_4$ decomposition with the time on stream of 22 and 29 h, respectively (magnification: 1000×).

The effect of structure modifier Zn could be seen also clearly from SEM images. As shown in Fig. 6, for the un-modified γ-Al$_2$O$_3$ the irregularly shaped γ-Al$_2$O$_3$ particles were transformed to disk-like and catalytically inactive crystalline α-Al$_2$O$_3$ in the CF$_4$ hydrolytic decomposition through the inter-action with the produced HF. The details of transformation mechanism of the γ-Al$_2$O$_3$ into α-Al$_2$O$_3$ could be seen more clearly from the reference [6]. However, the used 5% Zn/Al$_2$O$_3$

had less regularly shaped morphology than the pure γ-Al$_2$O$_3$ after long exposure to the environment of CF$_4$ decomposition, which was in good agreement with the results of BET and XRD measurements. That is, the spent 5% Zn/Al$_2$O$_3$ catalyst showed higher surface area and quite lower XRD intensities of α-Al$_2$O$_3$ peaks compared with the un-modified γ-Al$_2$O$_3$ catalyst after the reaction.

According to the results of activity and XRD measurements, 20% loading of Zn was enough to form mono-layer coverage of ZnAl$_2$O$_4$ on the γ-Al$_2$O$_3$ surface and make the catalyst resistant to the transformation of γ-Al$_2$O$_3$ into α-Al$_2$O$_3$.

In the fresh Ni/Al$_2$O$_3$ catalysts as calcined at 700 °C, γ-Al$_2$O$_3$ and NiSO$_4$ were the main phases (Fig. 7(A)). With the increase in nickel loading, the XRD peaks intensity of NiSO$_4$ became stronger. After CF$_4$ hydrolysis at 750 °C, instead of the NiSO$_4$ and γ-Al$_2$O$_3$ phases, NiAl$_2$O$_4$ together with α-Al$_2$O$_3$ peaks depending on the nickel loading appeared. As the nickel con-tent increased the intensity of α-Al$_2$O$_3$ peaks decreased and no α-Al$_2$O$_3$ phase was observed as the Ni content reached 15% by mole (Fig. 7(B)). As listed in Table 1, the surface area of Ni/Al$_2$O$_3$ as-prepared decreased with the increase in Ni loading but a reverse trend was found over the used catalysts similar to that of Zn/Al$_2$O$_3$ catalysts.

Table 1
BET surface area of γ-Al$_2$O$_3$ modified by Zn and Ni before and after CF$_4$ hydrolytic decomposition

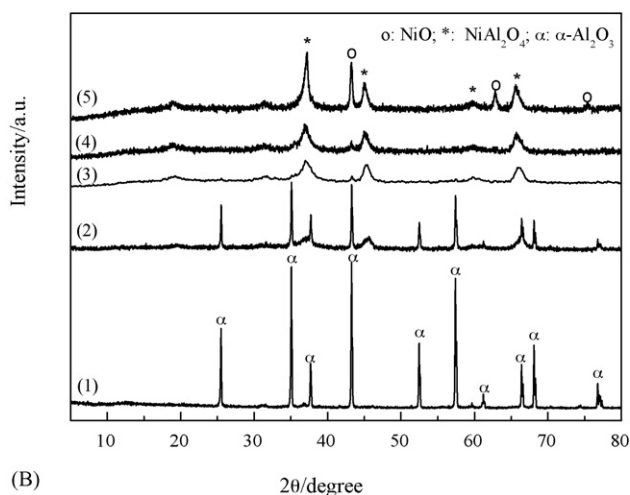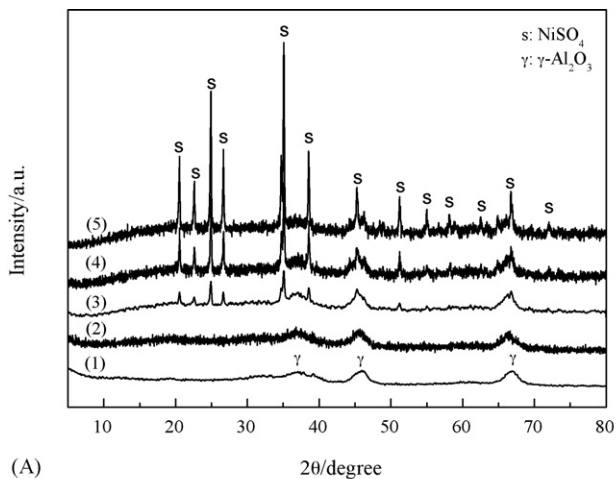| Catalysts	Surface area (m^2 g^{-1})		Used/fresh
	Fresh	Used	
γ-Al$_2$O$_3$	197.9	6.0	0.030
5% Zn/Al$_2$O$_3$	182.2	12.0	0.066
10% Zn/Al$_2$O$_3$	135.6	38.2	0.282
12% Zn/Al$_2$O$_3$	109.9	43.6	0.397
20% Zn/Al$_2$O$_3$	87.5	32.2	0.368
5% Ni/Al$_2$O$_3$	248.2	47.3	0.191
15% Ni/Al$_2$O$_3$	163.2	55.8	0.342
20% Ni/Al$_2$O$_3$	113.8	45.9	0.403
30% Ni/Al$_2$O$_3$	71.2	37.8	0.531

(A)

(B)

Fig. 7. XRD patterns of (A) fresh and (B) used Ni/Al$_2$O$_3$ with Ni mole percentage of (1) 0%, (2) 5%, (3) 15%, (4) 20% and (5) 30% (for the used catalysts, the reaction time could be seen from Fig. 4(B)).

Combining the results of characterization with catalytic activity of Zn/Al$_2$O$_3$ and Ni/Al$_2$O$_3$ catalysts, it can be proposed ZnAl$_2$O$_4$ and NiAl$_2$O$_4$ are efficient structure modifiers that can inhibit the transformation of the catalytically active γ-Al$_2$O$_3$ phase into a dense α-Al$_2$O$_3$ phase even in the presence of HF at high temperature.

Besides Zn and Ni, the possibility of alkaline earth metals as structure modifier for γ-Al$_2$O$_3$ was also evaluated. As shown in Fig. 8, the catalysts of Mg, Sr or Ba modified γ-Al$_2$O$_3$ presented lower initial conversion than un-modified γ-Al$_2$O$_3$ for the CF$_4$ decomposition, that is γ-Al$_2$O$_3$ > 2% Mg/Al$_2$O$_3$ > 2% Sr/Al$_2$O$_3$ > 2% Ba/Al$_2$O$_3$ > 10% Ba/Al$_2$O$_3$. It is indicated that the addition of alkaline earth metals to γ-Al$_2$O$_3$ brought a catalytically negative effect in activity. As can be seen in Fig. 9, only the γ-Al$_2$O$_3$ phase appeared in the Al$_2$O$_3$ modified by 2% alkaline earth metals, and BaAl$_2$O$_4$ became a dominant phase in 10% Ba/Al$_2$O$_3$ as prepared. After the CF$_4$ hydrolytic decomposition, the α-Al$_2$O$_3$ phase dominated the 2% Mg/Al$_2$O$_3$ but with a weaker intensity than the pure Al$_2$O$_3$ catalyst, while the γ-Al$_2$O$_3$ was a dominant phase in used 2% Sr/Al$_2$O$_3$ and 2% Ba/Al$_2$O$_3$, and only BaAl$_2$O$_4$ phase was seen in 10% Ba/Al$_2$O$_3$,

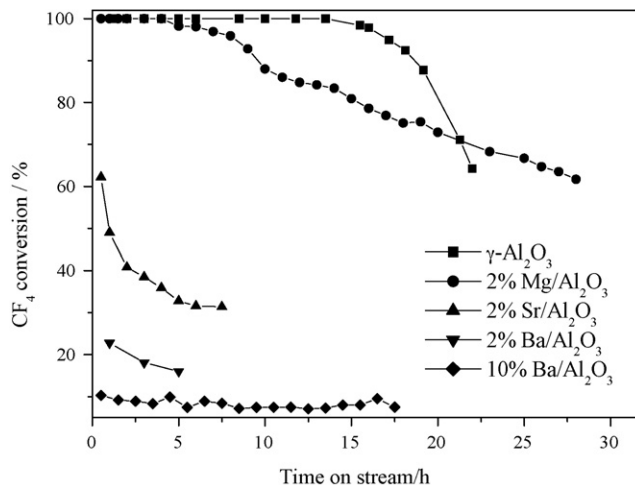Fig. 8. CF$_4$ hydrolytic conversion over Al$_2$O$_3$ modified by Mg, Sr and Ba.

as in their fresh state. As listed in Table 2, the used/fresh value of surface area shows the order of γ-Al$_2$O$_3$ < 2% Mg/Al$_2$O$_3$ < 2% Sr/Al$_2$O$_3$ < 2% Ba/Al$_2$O$_3$ < 10% Ba/Al$_2$O$_3$, which is consistent with their XRD results but opposite to the catalytic activity in the CF$_4$ decomposition.
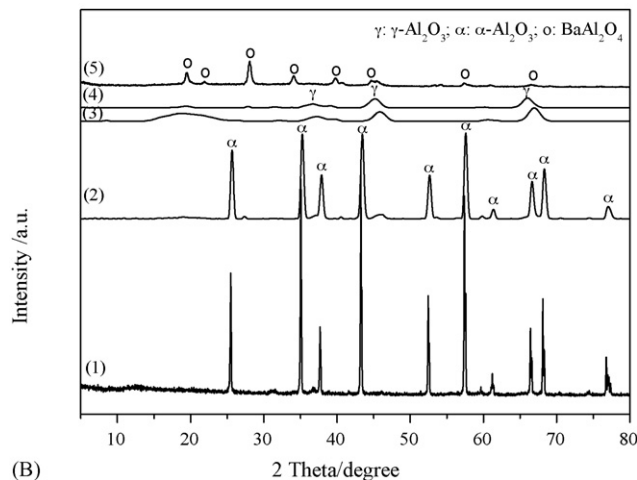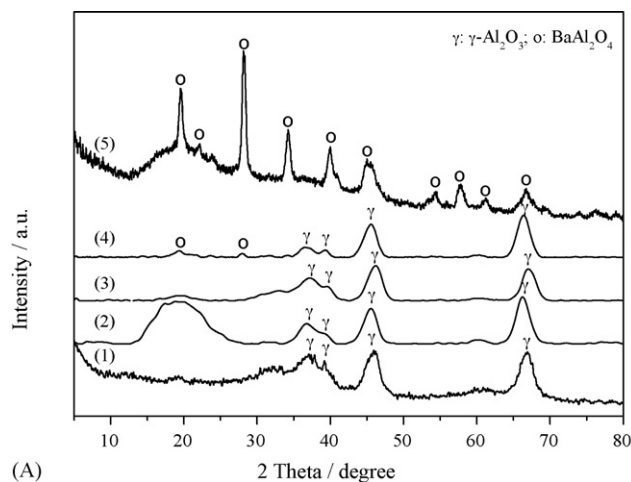

(A)

(B)

Fig. 9. XRD patterns of (A) fresh and (B) used catalysts: (1) γ-Al$_2$O$_3$, (2) 2% Mg/Al$_2$O$_3$, (3) 2% Sr/Al$_2$O$_3$, (4) 2% Ba/Al$_2$O$_3$ and (5) 10% Ba/Al$_2$O$_3$ (for the used catalysts, the reaction time could be seen from Fig. 8).

Table 2
BET surface area of γ-Al$_2$O$_3$ modified by alkaline earth metals as prepared and used in CF$_4$ hydrolysis

Catalysts	Surface area (m^2 g^{-1})		Used/fresh
	Fresh	Used	
2% Mg/Al$_2$O$_3$	226.7	19.7	0.087
2% Sr/Al$_2$O$_3$	209.2	158.2	0.756
2% Ba/Al$_2$O$_3$	219.6	183.2	0.834
10% Ba/Al$_2$O$_3$	122.7	104.8	0.854

The modification of γ-Al$_2$O$_3$ with alkaline earth metals reveals that they bring about a negative effect in the catalytic activity, but positively affected the structural stability through the formation of metal aluminates. According to the references on CFCs decomposition [18–25], it could be speculated that the catalytic performance of the modified γ-Al$_2$O$_3$ catalysts in the CF$_4$ decomposition has some correlation with their surface acidity. Therefore, the acidities of the catalysts as prepared and after the reaction were investigated by the FTIR spectra of adsorbed pyridine.

3.3. FTIR spectra of pyridine adsorbed on γ-Al$_2$O$_3$ based catalysts

Fig. 10 shows the FTIR spectra of pure and modified γ-Al$_2$O$_3$ in the fresh state after pyridine adsorption and evacuation at 100 °C. These spectra with adsorbed pyridine were obtained after subtraction with a spectrum taken just before pyridine adsorption. According to the references [26,27], the characteristic wave numbers of 1444, 1498, 1596 and 1611 cm^{-1} could be assigned to the pyridine species coordinatively adsorbed on Lewis acid sites while the 1545 cm^{-1} peak to the pyridinium ion formed on Brönsted acid sites. The fresh γ-Al$_2$O$_3$ revealed
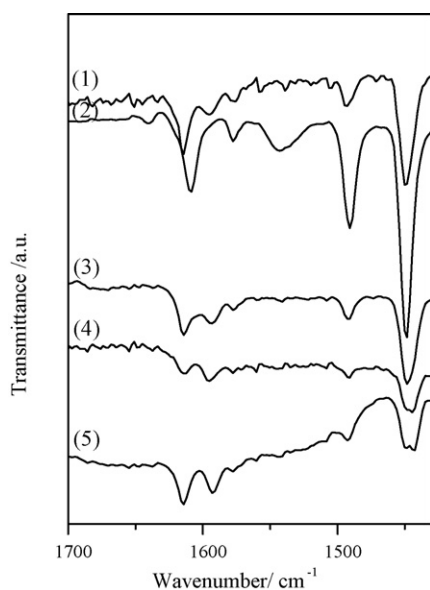

Fig. 10. FTIR spectra of pyridine adsorbed on fresh (1) γ-Al$_2$O$_3$, (2) 15% Ni/Al$_2$O$_3$, (3) 2% Mg/Al$_2$O$_3$, (4) 2% Sr/Al$_2$O$_3$ and (5) 2% Ba/Al$_2$O$_3$ after evacuation at 100 °C.
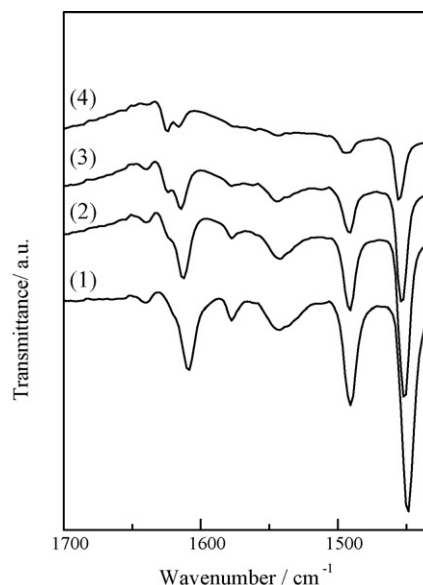

Fig. 11. FTIR spectra of pyridine adsorbed on fresh 15% Ni/Al$_2$O$_3$ after evacuation at (1) 100 °C, (2) 200 °C, (3) 300 °C and (4) 400 °C.

only Lewis acidity having peaks at 1445, 1590 and 1611 cm^{-1}. In the case of 15% Ni/Al$_2$O$_3$, not only the peaks attributable to Lewis acid sites, but also a band at 1543 cm^{-1} corresponding to Brönsted acid site was detected, which is mainly associated with the nickel species in the form of NiSO$_4$ and the existence of SO$_4{}^{2-}$ on catalyst surface [17]. In addition, 15% Ni/Al$_2$O$_3$ exhibited a large surface acidity amounts compared with bare γ-Al$_2$O$_3$, which is consistent with their activity in the steady state even though 100% conversion of CF$_4$ was obtained over both bare and Ni modified γ-Al$_2$O$_3$ at the beginning of reaction. The Mg, Sr and Ba modified Al$_2$O$_3$ showed only peaks at 1445, 1577, 1590 and 1611 cm^{-1} corresponding to the Lewis acid sites without Brönsted acid sites. Their intensities were also lower than that of bare γ-Al$_2$O$_3$. It is thought that the decreased acidity is the main reason for the decreased CF$_4$ decomposition activities over the γ-Al$_2$O$_3$ modified with alkaline earth metals. That is, the modification of γ-Al$_2$O$_3$ with alkaline earth metals such as Mg, Sr and Ba brings about an improvement in catalyst stability by the formation of metal aluminates, but reduces hydrolysis activity by neutralizing Lewis acid sites of γ-Al$_2$O$_3$. Consequently, it can be concluded that Ni is an efficient structure modifier to stabilize γ-Al$_2$O$_3$ but alkaline earth metals are not suitable ones.

The acidic properties of Ni modified γ-Al$_2$O$_3$ catalysts were thoroughly investigated in the following experiments. Fig. 11 shows the FTIR spectra of pyridine adsorbed on the fresh 15% Ni/Al$_2$O$_3$ catalyst and evacuated at 100–400 °C. The acid sites were quite strong and pyridine peaks were detected even after evacuation at 400 °C.

The function of Ni modifier could be seen more clearly on the used catalysts. As shown in Fig. 12, most of acid sites over the bare γ-Al$_2$O$_3$ disappeared after 22 h of time on stream. However, it was modified with Ni considerable amount of Lewis acid sites still existed even after 47 h of time on stream, but the Brönsted acid sites disappeared, which is in accordance with the nickel
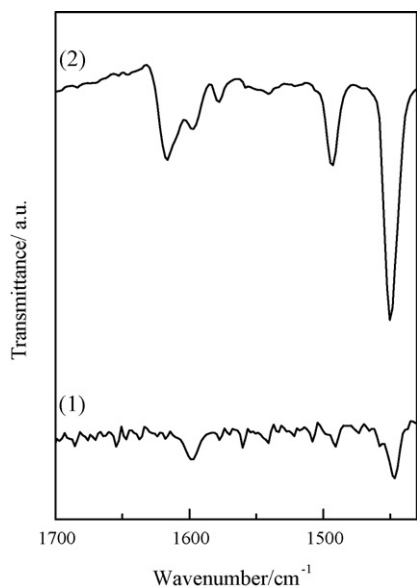
Fig. 12. FTIR spectra of used (1) γ-Al$_2$O$_3$ and (2) 15% Ni/Al$_2$O$_3$ after pyridine adsorption and evacuation at 100 °C (the reaction time of γ-Al$_2$O$_3$ and 15% Ni/Al$_2$O$_3$ was 22 and 47 h, respectively).

species in the form of NiAl$_2$O$_4$ rather than NiSO$_4$ in used 15% Ni/Al$_2$O$_3$. Similarly, the Lewis acid sites on Zn/Al$_2$O$_3$ resistant to HF at high temperature can also be seen from FTIR spectra of pyridine adsorbed on used 10% Zn/Al$_2$O$_3$ catalyst, which was reported in our previous paper [6]. These results reveal that the Lewis acidity of γ-Al$_2$O$_3$ based catalysts plays an important role in the CF$_4$ hydrolytic decomposition and the efficient structure modifier can firmly preserve the Lewis acid sites in a corrosive environment of HF at high temperature.

4. Conclusions

γ-Al$_2$O$_3$ obtained by calcining boehmite was an efficient catalyst for CF$_4$ hydrolytic decomposition. However, the transformation of γ-Al$_2$O$_3$ into α-Al$_2$O$_3$ effected by the produced HF resulted in a rapid loss of surface acidity and hence its activity. When Zn or Ni as a structure stabilizer was introduced into the γ-Al$_2$O$_3$, its catalytic stability could be enhanced by the formation of ZnAl$_2$O$_4$ or NiAl$_2$O$_4$ resistant to HF. Alkaline earth metals such as Mg, Sr and Ba were also good structural stabilizers for γ-Al$_2$O$_3$ but the catalytic activity of resulting catalysts for the CF$_4$ decomposition was decreased due to the neutralizing effect on the acid sites of γ-Al$_2$O$_3$. The hydrolytic decomposition of CF$_4$ is an acid catalyzed reaction, the Lewis acidity of γ-Al$_2$O$_3$ based catalysts plays an important role and the efficient structure

modifier can firmly preserve the Lewis acid sites on catalysts in the CF$_4$ decomposition process.

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