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Hydrolytic decomposition of CF_4 over alumina-based binary metal oxide catalysts: high catalytic activity of gallia-alumina catalyst

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Abstract

The hydrolytic decomposition of CF_4 has been conducted on gallia promoted alumina (Ga-Al oxide) catalysts at 803–903 K and 0.1 MPa. Steady state activity on 20% Ga-Al oxide was 15 times of that on Ce10%-$AlPO_4$ catalyst, on which the highest activity has been reported. The catalytic activity was further improved by incorporation of sulfate anion in Ga-Al oxide and by applying sol–gel method in preparation of the catalyst. XRD spectra of Ga-Al oxides showed a shift of diffraction peaks assigned to γ-alumina toward lower angles, indicating the formation of gallia-alumina solid solution. In situ FT-IR of pyridine adsorption spectra of Ga-Al oxides showed peaks solely attributable to Lewis acid (L-acid) sites at 1445–1455, ca. 1495, 1577, ca. 1594, and ca. 1622 cm^{-1}. The steady state catalytic activities increased with increasing peak areas at 1446 or 1622 cm^{-1} of Ga-Al oxides with various Ga%, suggesting participation of Lewis acid sites into the reaction. It is demonstrate from surface area measurements of Ga-Al oxide catalyst before and after the reaction that not only higher catalytic activity but also higher catalyst stability were observed on Ga-Al oxide, Ga-Al oxide with sulfate, and Ga-Al oxide prepared by sol–gel method than on their parent oxides of alumina, Ga-Al oxide, and Ga-Al oxide prepared by incipient wetness method, respectively.
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1. Introduction

Carbon tetrafluoride (CF_4) and carbon hexafluoride (C_2F_6) are by-products of the primary aluminum production process, and have been utilized as etching and cleaning agents in integrated circuit production. A large part of these perfluorocarbons (PFCs) is escaping into atmosphere. However, these are potent greenhouse gases, with global warming potentials of approximately 6500 and 9200 times that of CO_2, respectively, and have lifetimes that exceed 10,000 years. Therefore, the decomposition of these gases is a very important subject in the present environmental research works. The toughness of C–F bond ($543 \pm 4\,\text{kJ mol}^{-1}$) [1] makes the decomposition of CF_4 a very hard task. Within many methods used for the decom-

position of PFCs [2–6], the catalytic decomposition may be the best choice because that the decomposition can be operated under mild reaction conditions, which avoid the production of hazardous products such as dioxin. Among reported literatures, $AlPO_4$-based catalysts such as 10%Ce loaded $AlPO_4$ and $AlPO_4/SiO_2$, are found to be the most reactive catalysts [7–9]. It was demonstrated in our previous paper that catalytic activity in the hydrolytic decomposition of CF_4 on 5% Ga loaded alumina catalyst was higher than that of 10%Ce-$AlPO_4$ catalyst [10].

To further increase the catalytic activity of CF_4 hydrolysis, the effect of Ga loading in alumina on the activity was examined in this paper. Change in catalytic activity with amount of Ga loading in Ga-Al oxide catalyst is related with formation of Al-Ga bimetallic oxide solid solution, similarly as in the case of NO reduction [11–17], dehydroaromatization of *n*-butane [18], and hydrodesulfurization of thiophene [19]. The activity of Ga-Al oxide catalysts was also correlated with TPR-TG-Mass data, surface area, and acidic characters as in the case of decomposition of chlorofluorocarbons [20–23]. Effect of treatment with H_2SO_4 and method of catalyst preparation on catalytic activity was also examined.

2. Experimental

2.1. Catalyst preparation

A series of gallia-alumina binary metal oxide (Ga-Al oxide) catalysts was prepared by incipient wetness method from boemite alumina (Catapal A, Vista Chemical Co.) with an aqueous solution of $Ga(NO_3)_3 \cdot 8H_2O$ at room temperature, followed by drying overnight at 393 K. The resulting solid was crushed, sieved into 20–40 meshes, and calcined in air at 873–1073 K for 5 h. Ga-Al oxide catalysts promoted with such acids as sulfuric acid, hydrofluoric acid, and phosphoric acid, were prepared similarly except that aqueous acid solutions plus $Ga(NO_3)_3 \cdot 8H_2O$ was used in the place of aqueous $Ga(NO_3)_3 \cdot 8H_2O$ solution. Ga-Al oxide catalysts were also prepared by using sol–gel method in ethylene glycol as solvent. The prepared gallia-alumina and its sulfate promoted catalysts will be referred as Gax and GaxSy, respectively, where x and y stand for Ga/(Ga + Al) and SO_4^{-2}/(Al + Ga) molar%, respectively.

2.2. Catalytic reaction

The hydrolytic decomposition of CF_4 was carried out under atmospheric pressure using a continuous flow reaction system with a fixed-bed reactor, as described previously [10]. A gas mixture of CF_4/N_2/steam (0.1/9.9/5.1) was passed over 0.5 g of the catalyst at a total flow rate of 15.1 ml min^{-1}, unless otherwise stated. The gas effluent from the reactor was washed by distilled water to remove HF formed, and then the gas was analyzed by a TCD gas chromatograph (8 A, Shimadzu Co.) equipped with a 2 m Unibeads C column. The activity of the catalyst in the CF_4 hydrolysis will be expressed in conversion % of CF_4 or in volume of converted CF_4 per time and catalyst weight (ml min^{-1} g^{-1}), which was calculated from (conversion %)/100 × (flow rate of CF_4)/(catalyst weight).

2.3. Catalyst characterization

FT-IR spectra of pyridine adsorbed at room temperature and evacuated at 473 K for 30 min on the catalyst after the hydrolysis reaction were recorded by use of an FT-IR instrument (8100 M, Shimadzu Co.). Data were processed by using software of GRAMS/32 AI, version 6. Temperature programmed reaction (TPR) experiment of fluorinated catalysts with water vapor were carried out by using a TG-DTA-Mass instrument (Model 2000S, Mac Science Ltd.). The fluorinated catalyst was prepared by the reaction of fresh catalyst with HF in flowing helium stream of 10 ml min^{-1} for 4 h at ambient temperature. Mass spectra were obtained in a range from 1 to 150 m/e in every 1.5 s. Temperature was increased linearly from ambient to 1273 K at a ramping rate of 10 K min^{-1}. X-ray diffraction (XRD) pattern of fresh and used catalysts was measured in a 2θ range from 10 to 70° on an XRD instrument (DMX/III-VC,

Rigaku Denki Co.) using Cu Kα radiation. Surface area of catalyst before and after the reaction was determined by the BET method using OMNISORP 100CX (Beckman Coulter Co.).

3. Results and discussion

3.1. Change in catalytic activity of the CF_4 hydrolysis reaction with calcination temperature and Ga loading of Ga-Al oxide catalysts

Ga-Al oxide catalysts with different Ga/(Ga + Al) ratio in the range of 3–50% were prepared, and tested for the hydrolysis reaction of CF_4. Fig. 1 presents effect of calcination temperature of Ga20 catalyst on the catalytic activity. Initial high catalytic activity decreased rapidly in several hours of time on stream, and the activity became steady after 3–4 h of time on stream. Hereafter, a steady state activity will be referred to that obtained after 5 h of time on stream. The highest steady state activity was obtained when Ga20 catalyst has been calcined at 973 K, which will be used as a standard calcination temperature.

The steady state conversion % of CF_4 as a function of Ga loading is shown in Fig. 2. At 903 K, the catalytic activity on Ga-Al oxide catalyst increased gradually with increasing Ga loading from 64% on bare alumina to 82–88% on Ga20–Ga40, and then decreased rapidly with further increase of Ga loading. Similarly, at 853 K, the conversion % increased gradually from 24% over bare alumina to 70% over Ga20, and decreased by further addition of Ga. On the other hand, only 39% of CF_4 was decomposed on a physical mixture of gallium oxide and aluminum oxide having the Ga/(Ga + Al) ratio of 20% at 853 K.

It is worth to mention that Ga-Al oxide catalysts have higher catalytic activity than that reported previously, as listed in Table 1. A comparison of the catalytic activities was made using a common unit of ml min^{-1} g^{-1} but not conver-
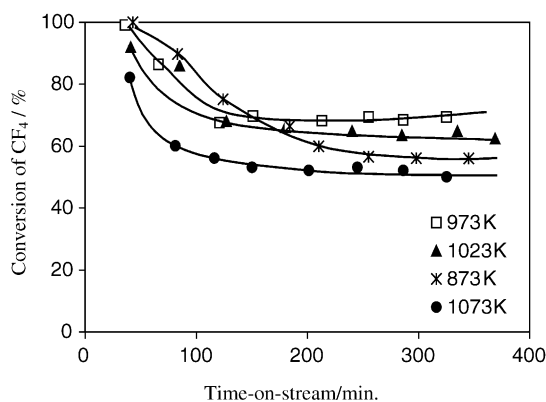

Fig. 1. CF_4 conversion % in the hydrolysis reaction as a function of time-on-stream over Ga20 calcined at different temperatures under the reaction conditions of 853 K, 0.5 g of catalyst and H_2O/CF_4 = 51.
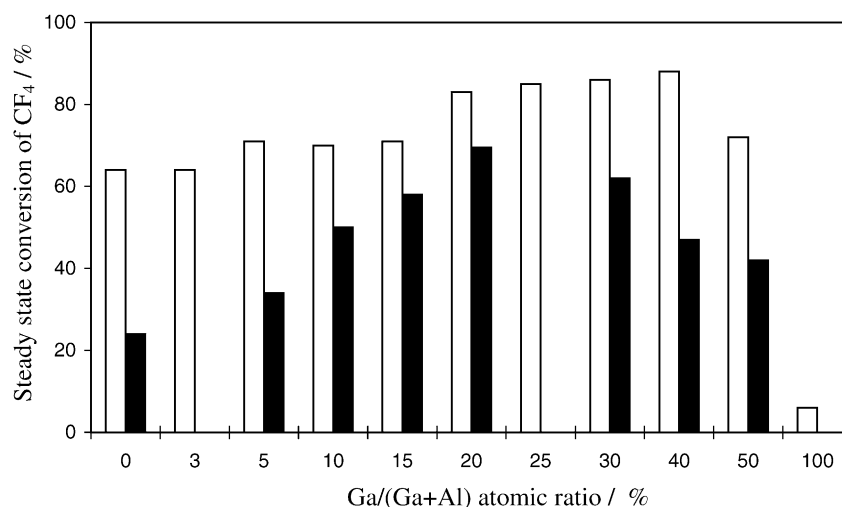
Fig. 2. Steady state activity in the CF_4 hydrolysis reaction over Ga-Al oxide catalysts with various Ga loadings at 853 K (■) and 903 K (□).

Table 1
Comparison of the catalytic activities[a] described in this paper to the previous literatures

Temperature (K)	Catalysts				
	Ce10%-AlPO$_4$[b]	15%Ni-Al oxide[c]	Ga20	Ga20S5	Ga20-EG[d]
753	0		0.03/16	0.06/26	0.07/36
803	0		0.07/33	0.11/57	0.15/75
853	0.01[e]/20	0.11[e]/89	0.14/69	0.16/82	0.17/86
903	0.02[f]/44	0.12[f]/99	0.17/82	0.20/98	0.20/98
973	0.03/90				

[a] Catalytic activities were expressed in ml min^{-1} g^{-1} and conversion % of CF_4.
[b] Ref. [7].
[c] Ref. [24].
[d] Prepared by sol–gel method in ethylene glycol.
[e] At 873 K.
[f] At 923 K.

sion % of CF_4, which was also shown in Table 1. At 853 K, the hydrolysis reaction on Ga20 proceed about 15 times faster than that on Ce10%-AlPO$_4$ catalyst reported by Takita et al. [7–8]. Even it surpasses 1.3 times to that on Ni-Al oxide catalyst reported in a patent literature [24]. Addition
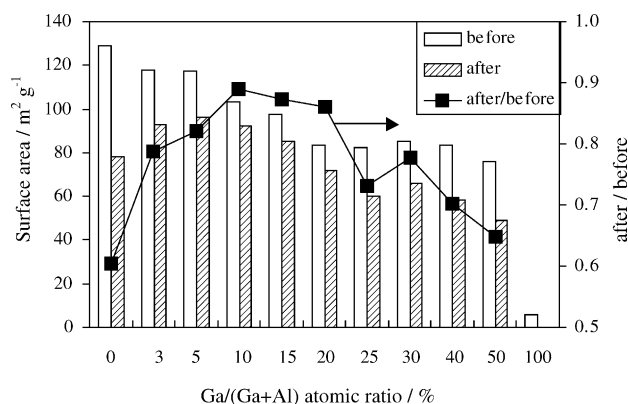

Fig. 3. Surface area of Ga-Al oxide catalyst with various Ga loadings before and after the reaction for 5 h at 853 K, and their ratios.

of Ga to alumina not only increases their catalytic activities in the hydrolysis of CF_4 but also stabilizes the catalyst surface. Fig. 3 shows the surface area of as-prepared and used Ga-Al oxide catalysts as a function of various Ga loadings. Surface area of all the Ga-Al oxide catalysts decreased after the reaction. Notably, parent alumina lost a half of its surface area during the CF_4 hydrolysis reaction whereas 5–20% Ga-loaded Ga-Al oxide catalysts missed only 12–18% of their original surface areas after the reaction. Steady state activity divided by surface area of the catalyst gradually increased with increasing Ga loading in Ga-Al oxide catalyst, and then leached to a plateau at above 20% Ga loading, suggesting formation of active phase for the CF_4 hydrolysis reaction by Ga-oxide addition to alumina.

3.2. Characterization of Ga-Al oxide catalysts

To find out the active phase for the reaction, XRD studies were conducted. XRD spectra of Ga promoted alumina with different Ga-loadings in the range of 0–50% are shown in Fig. 4. These spectra were measured for samples after being
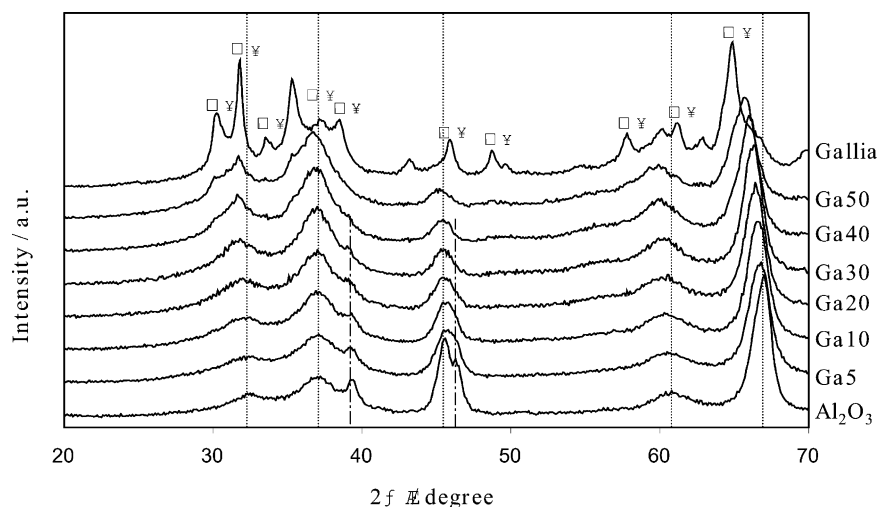
Fig. 4. XRD pattern of Ga-Al oxide catalyst with various Ga loadings after being used in the CF$_4$ hydrolysis reaction, (▼) for Ga$_2$O$_3$ and lines for alumina.

used in the CF$_4$ hydrolysis for 5 h. As shown in Fig. 4, the spectrum of alumina consisted of seven broad peaks centered at around 66.7, 60.6, 46.5, 45.9, 39.5, 37.4, 32.6° of 2θ. Within these peaks, five peaks at 66.7, 45.9, 37.4, 60.6, 32.6° in decreasing order of peak height can be assigned to γ-Al$_2$O$_3$ as compared to a data file PDF#50–0741, which gives five peaks at 66.6, 45.7, 37.5, 60.5, 31.9° in decreasing order of peak height. The other two peaks at $2\theta = 46.5$ and 39.5° may come from a phase, which often accompanies with γ-Al$_2$O$_3$, as seen in a data file PDF#47–1308. Heights of these extra peaks at 39.5 and 46.5° decreased, and disappeared with increasing Ga loading in alumina. At the same time, peak position of all other five peaks attributable to γ-Al$_2$O$_3$ shifted to lower angles by the addition of Ga up to 40% in alumina, suggesting the replacement of Al by Ga and the formation of γ-(Al-Ga)$_2$O$_3$ solid solution. Formation of Al-Ga oxide solid solution has been reported in literatures [14,16,17,25,26]. Further addition of Ga in alumina gave rise peaks assigned to Ga$_2$O$_3$ of PDF#41–1103 together with peaks of the solid solution, as shown in Fig. 4. It may be concluded from above results that the increase in the catalytic activity by the Ga addition into alumina may be attributed to the formation of γ-(Al-Ga)$_2$O$_3$ solid solution and Ga-O-Al linkage.

Hydrolysis activity of chlorofluorocarbons has often been correlated with acidic characters of the catalysts [20–23]. Accordingly, acidic properties of Ga-Al oxide catalyst were estimated from in situ FTIR measurements of adsorbed pyridine. Fig. 5 shows IR spectra of pyridine adsorbed on Ga-Al oxides with different Ga loadings after being used in the CF$_4$ hydrolysis reaction for 5 h. Spectra were recorded over a frequency range of 1700–1400 cm^{-1}, where characteristic vibration modes of adsorbed pyridine will appear. It is well known that pyridine adsorbed on Lewis acid (L-acid) sites gives bands at 1440–1460, 1488–1503, ≈1577, 1590–1600, and 1600–1633 cm^{-1}, that on Brönsted acid (B-acid) sites at 1485–1500, 1540, and 1630–1650 cm^{-1} and the hy-drogen bonded pyridine at 1400–1447, 1485–1490, and 1580–1600 cm^{-1} [27–36]. Upon evacuating the sample at 473 K for 30 min, no peaks corresponding to H-bonded pyridine or B-acid sites were detected in the spectra of all samples while five bands assigned to L-acid sites were detected at 1440–1460, ca. 1495, 1577, 1594, and 1610–1630 cm^{-1}. Peak heights of all the peaks except for that at 1577 cm^{-1} increased with increasing Ga loading up to 10–30% in alumina, and then decreased. Notably new peaks at ca. 1594 and 1446 cm^{-1} appeared on Ga-Al oxide with 10–30% Ga loading. These changes may come from pyridine adsorbed on the Ga-Al oxide solid solution and Ga-O-Al linkage. In further analysis, a group of peaks at 1440–1460 and 1610–1630 cm^{-1} was deconvoluted into three peaks each, respectively. Table 2 shows areas of the peaks at 1446 and 1662 cm^{-1} obtained after the curve fitting. These peak areas increased up to 20% of Ga loading, and then decreased with increasing Ga content in alumina. Change in the peak areas with Ga loading in alumina exactly matches with that in the catalytic activities of CF$_4$ hydrolysis reaction, as shown in Fig. 2. These results strongly suggest that L-acid sites formed on γ-(Al-Ga)$_2$O$_3$ solid solution participate in the hydrolytic decomposition of CF$_4$.

Table 2
Peak area of Ga-Al oxide with various Ga loadings obtained by curve fitting of FT-IR spectra in the range of 1440–1460 and 1610–1630 cm^{-1}

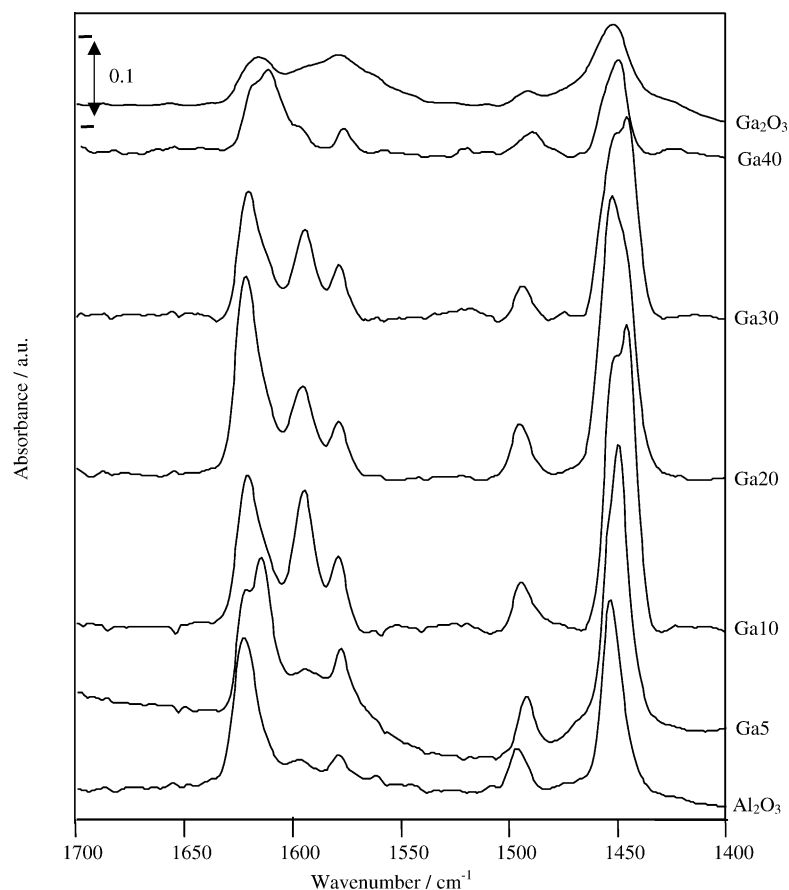| Catalyst	Wave number (cm^{-1})	
	1446	1622
Al$_2$O$_3$	None	1.5
Ga5	0.6	1.4
Ga10	2.4	1.9
Ga20	2.8	3.4
Ga30	2.6	2.0
Ga40	0.4	1.5
Ga$_2$O$_3$	None	0.5

Fig. 5. In situ FT-IR spectra of pyridine adsorbed on Ga-Al oxide with various Ga loadings after being used in the CF$_4$ hydrolysis reaction.

As shown in Fig. 1, the catalytic activity in the CF$_4$ hydrolysis on Ga20 varies with calcination temperature, being a maximum at 973 K of the calcination temperature. Fig. 6 shows IR spectra of adsorbed-pyridine on Ga20, which have been calcined at 873, 973, and 1073 K, and then used in the hydrolysis of CF$_4$ for 5 h. All the spectra showed only peaks characteristic to L-acid sites centered at 1622, 1595, 1577, 1495, and 1454 cm^{-1}. The peak intensities of these five peaks became maximum when the catalyst has been calcined at 973 K, being exactly same tendency as the catalytic activity. Table 3 shows the change in peak areas at 1446 and 1662 cm^{-1} with the calcination temperatures as typical examples. On the other hand, XRD spectra of these catalysts showed the monotonous increase in intensities of all peaks

Table 3
Peak area of Ga20 calcined at different temperatures obtained by curve fitting of FT-IR spectra at 1454 and 1622 cm^{-1}

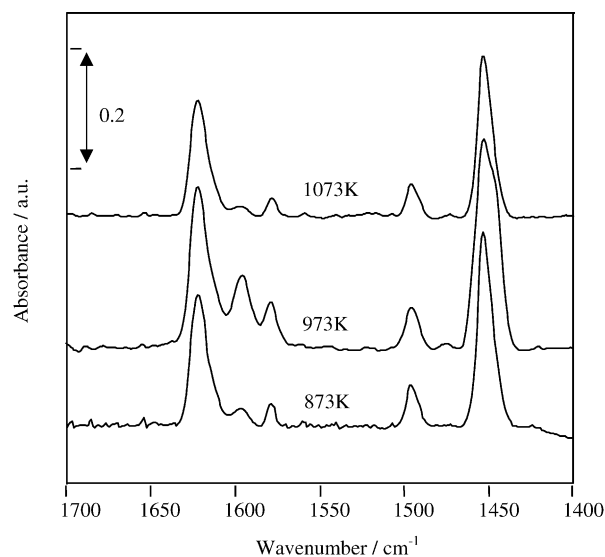| Calcination temperature (K)	Wave number (cm^{-1})	
	1454	1622
873	3.4	2.7
973	5.4	3.4
1073	2.8	2.3

Fig. 6. In situ FT-IR spectra of pyridine adsorbed at ambient temperature and evacuated at 473 K on Ga20 catalyst calcined at different temperatures of 873, 973, and 1073 K (from bottom to top).
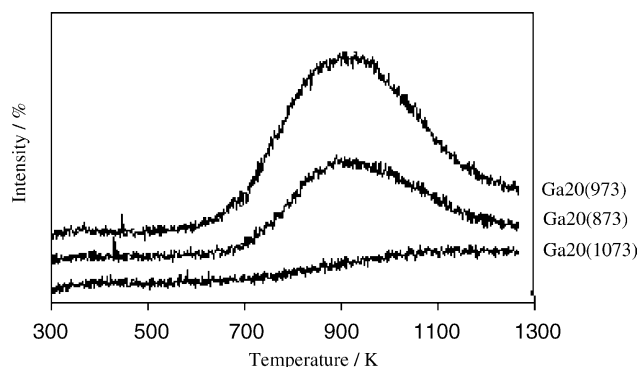
Fig. 7. TPR-Mass spectra at $m/e = 20$ of fluorinated Ga20, which has been calcined at different temperatures.
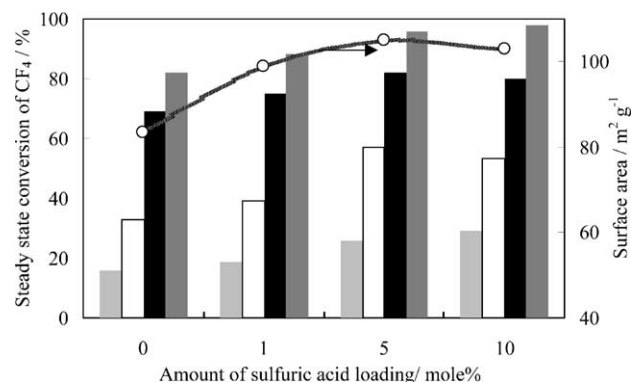

Fig. 8. Effect of loading amount of sulfuric acid in Ga20 catalyst on the catalytic activity and surface area as a function of reaction temperature; gray, white, black, and dark gray columns for 753, 803, 853, and 903 K, respectively.

with increasing calcination temperature. These results once again suggest that L-acid sites formed on γ-(Al-Ga)$_2$O$_3$ solid solution participate in the CF$_4$ hydrolysis reaction.

The hydrolysis of CF$_4$ may pass through two steps, which are fluorination of the surface by CF$_4$ and hydrolysis of surface fluoride with water to recover surface oxides [10]. The surface metal fluorides produced on binary metal oxide catalysts by the reaction with HF at ambient temperature for 5 h were hydrolyzed with water, and the products were analyzed by a mass spectrometer, as explained in the experimental section. Fig. 7 shows the effect of the calcination temperature of Ga20 on the peak height of HF ($m/e = 20$) versus reaction temperature. The area under the curve reflects the amount of released HF as a function of temperature. The area under curves was calculated, and found to be 35, 18, and 6 in an arbitrary unit for Ga20 calcined at 973, 873, and 1073 K, respectively. The area under peaks decreased in the same order as the amount of L-acid sites and the steady state catalytic activity. These data demonstrate the role of L-acid sites [10], that is, the catalysts having higher amount of L-sites accommodate more F on the surface, and hence larger number of CF$_4$ molecules decomposed. The fluorinated surfaces are easily hydrolyzed by water to recover the original surface.

3.3. Catalyst pre-treated with different acids and prepared by sol–gel method

It has been reported that the acidic and catalytic properties of metal oxides were greatly affected by pre-treatment with sulfuric, hydrofluoric, and phosphoric acids [37–43]. Ga20 catalysts treated with these acids were prepared and used for the CF$_4$ hydrolysis reaction. The steady state conversions at 903 K were obtained to be 32, 44, and 93% on Ga20 with 5 mol% hydrofluoric, phosphoric, and sulfuric acid, respectively, in comparison with 84% on the parent Ga20 catalyst. It is apparent that pre-treatment of Ga20 catalyst with sulfuric acid was a promising method for improving the catalytic activity, and then the additional experiments were conducted.

Fig. 8 shows the steady state activity in the CF$_4$ hydrolysis reaction over sulfuric acid-treated Ga20 catalysts with regard

to reaction temperature. The amount of H$_2$SO$_4$ added in Ga20 was set to 1, 5, and 10 mol%. The highest catalytic activity was obtained on Ga20 with 5–10 mol% H$_2$SO$_4$ at all the reaction temperatures examined. A similar tendency has been reported in the ethylene dimerization reaction over NiO–TiO$_2$ treated with sulfuric acid. [43].

The life of the catalyst is one of the most important factors for a preferable catalyst, especially from the viewpoint of practical usage. As shown in Fig. 9, Ga20 catalyst with sulfuric acid not only promotes the CF$_4$ hydrolysis reaction at high catalytic activity but also keeps the high catalytic activity for long time on stream. CF$_4$ was hydrolyzed 98% at the initial stage of reaction, and maintained that level for more than 3 days at 903 K on Ga20S10. Even at such low temperature as 803 K, conversion % keeps at 57% level for 100 h.

As stated, the catalytic activity of Ga20 prepared by incipient wetness method was about 15 times of that on Ce10%-AlPO$_4$, on which the highest activity has been reported [7–8]. Even, the catalytic activity of Ga20 exceeded more than 30% of that on 15% Ni-Al oxide catalyst from a patent literature [10]. H$_2$SO$_4$-modified Ga20 and Ga20
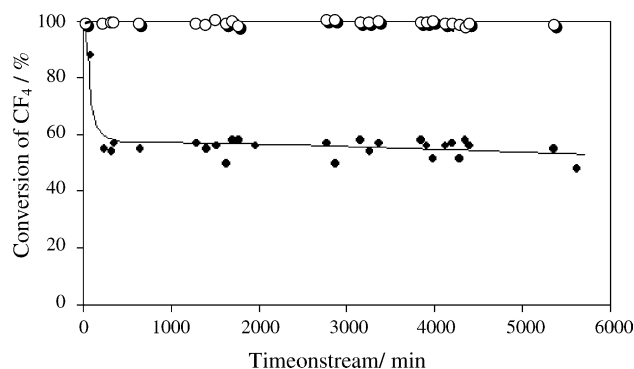

Fig. 9. Long time on stream experiment on the catalytic activity of 5 mol% (●) and 10 mol% (○) H$_2$SO$_4$ added Ga20 catalysts as a function of time-on-stream at 803 K (●) and 903 K (○).

Table 4
Peak area at 1454 and 1622 cm^{-1} of FT-IR of pyridine adsorbed on Ga20 added with different amount of sulfuric acid

Catalyst	Wave number (cm^{-1})		
	1454[a]	1622[a]	1550[b]
Ga20	5.4	3.4	0
Ga20S1	5.3	3.7	0.1
Ga20S5	6.3	4.2	0.9
Ga20S10	7.4	4.2	0.9

[a] For L-acid.
[b] For B-acid.

prepared by sol–gel method promote the reaction much higher rate than Ga20 prepared by incipient wetness method does, as demonstrated in Table 1. The catalytic activity of the standard Ga20 prepared by incipient wetness method increased 1.7 times by the addition of sulfate, and 2.3 times by applying sol–gel method at 753–803 K of reaction temperature.

The addition of sulfuric acid to Ga20 should change acidic properties of Ga20. FT-IR spectra of pyridine adsorbed on H_2SO_4-added Ga20 catalysts were measured after being used in the CF_4 hydrolysis reaction for 5 h. Beside the bands for L-acid sites at 1454, 1495, 1577, and 1622 cm^{-1}, two peaks at 1540–1550 and at 1630–1640 cm^{-1} assigned to B-acid sites were detected, which are not present on none-treated Ga20. The area under representative peaks for L-acid sites at 1454 and 1622 cm^{-1}, and for B-acid sites at 1550 cm^{-1} were calculated and listed in Table 4. All the peak areas monotonously increased with increasing the amount of sulfuric acid added to Ga20. These results may suggest that the acid sites created by sulfuric acid addition to Ga20 could not serve as the active sites for the CF_4 hydrolysis reaction. It was observed from XRD studies that the introduction of sulfuric acid to Ga20 led to an overall decrease in the intensity and broadening of all the peaks. Such decrease and broadening in the peak intensity was accompanied by an increase in the surface areas of sulfuric acid treated Ga20 catalysts before being used for the CF_4 hydrolysis reaction, as shown in Fig. 8. The increase of the surface area may be the main reason for increasing the catalytic activity. As was stated in Section 3.1, the addition of Ga to alumina stabilized the catalysts surface. The addition of sulfuric acid to Ga20 further stabilized the catalyst surface during the CF_4 hydrolysis reaction. Similar stability increase by the sulfuric acid treated TiO_2, SnO_2, and Fe_2O_3 was reported during the CFC-12 decomposition [40].

4. Conclusions

Catalytic activity of alumina in the hydrolytic decomposition of CF_4 increased by the addition of gallia, and maximized at 10–20 mol% addition of gallia to alumina, where the catalytic activity became more than three times to the parent alumina and 15 times to Ce10%-$AlPO_4$ catalyst.

XRD analysis of Ga-Al oxide revealed the formation of bimetallic solid solution, and peak height of the bimetallic solid solution increased with increasing gallia content up to 20% in alumina. In addition, FT-IR of pyridine adsorption on catalyst showed only L-acid sites, and amount of L-acid sites increased with increasing gallia content up to 20% in alumina. Therefore, the catalytic activity of gallia-alumina catalysts was directly correlated with the amount of L-acid sites and solid solution of Ga-Al bimetallic oxide, suggesting the linkage Ga-O-Al as the new active sites. Gallia addition in alumina not only increased the catalytic activity but also stabilized the surface area during the hydrolytic decomposition of CF_4.

The catalytic activity of Ga20 was further improved by incorporation of sulfate and by use of sol–gel method for preparation of Ga20. The catalytic activity increased 1.7 and 2.3 times by the former and the latter methods, respectively, at 753–803 K of reaction temperature.

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