

Article

Effects of Sulfuric Acid Treatment on the Performance of Ga-Al₂O₃ for the Hydrolytic Decomposition of 1,1,1,2-Tetrafluoroethane (HFC-134a)

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Abstract: HFC-134a, one of the representative hydrofluorocarbons (HFCs) used as a coolant gas, is a known greenhouse gas with high global warming potential. Catalytic decomposition is considered a promising technology for the removal of fluorinated hydrocarbons. However, systematic studies on the catalytic decomposition of HFC-134a are rare compared to those for other fluorinated hydrocarbon gases. In this study, Ga-Al₂O₃ and S/Ga-Al₂O₃ catalysts were prepared and the change in their properties post-acid treatment was investigated by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), temperature-programmed desorption of ammonia (NH₃-TPD), in situ Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDS), and X-ray photoelectron spectroscopy (XPS). The S/Ga-Al₂O₃ catalyst achieved a much higher HFC-134a conversion than Ga-Al₂O₃, which was ascribed to the promotional effect of the sulfuric acid treatment on the Lewis acidity of the catalyst surface, as confirmed by NH₃-TPD. Furthermore, the effect of hydrogen fluoride (HF) gas produced by HFC-134a decomposition on the catalyst was investigated. The S/Ga-Al₂O₃ maintained a more stable and higher HFC-134a conversion than Ga-Al₂O₃. Combining the results of the stability test and characterization, it was established that the sulfuric acid treatment not only increased the acidity of the catalyst but also preserved the partially reduced Ga species.

Keywords: 1,1,1,2-tetrafluoroethane (HFC-134a); chlorofluorocarbon; catalytic decomposition; Ga-Al₂O₃; Lewis acid site

1. Introduction

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are two classes of coolants, which have been found to directly contribute to the destruction of the stratospheric ozone layer [1,2]. The Montreal protocol in 1987 banned the use of these coolants, and hydrofluorocarbons (HFCs) were developed to replace them [1,2]. With the increase in use of air conditioning, the concentration of HFCs in the atmosphere has risen significantly [1–3]. HFCs do not deplete the ozone layer, but as greenhouse

gases, their global warming potential is ~12,000 times higher than that of CO₂ [1,3]. HFC-134a is one of the most commonly used HFC refrigerants today, and measures to remove it from the atmosphere are urgently required to prevent global warming [1].

Several technologies, such as thermal decomposition, plasma, and catalytic decomposition, have been investigated for HFC-134a removal [4–9]. Among these methods, catalytic decomposition is considered promising because it can be carried out at lower temperature than other methods [7–9]. Izuka et al. experimentally compared thermal and catalytic decompositions [9]. For thermal decomposition, the initiating temperature for decomposition of HFC-134a was higher than 750 °C, and complete conversion was obtained at 900 °C [5,9]. On the other hand, using waste cement as a catalyst, 100% conversion of HFC-134a was achieved at about 600 °C [9].

Various catalysts, such as waste concrete, supported catalysts, and metal phosphate catalysts, have been investigated [7–10]. Alumina (Al₂O₃)-based catalysts have been commonly applied for the decomposition of HFC-134a because Al₂O₃ is inexpensive and a representative acid catalyst [8,10]. Han et al. reported that an Al₂O₃-based catalyst exhibits a very high activity and showed a higher stability when using water as a hydrogen donor. Swamidoss et al. tested the catalytic decomposition of HFC-134a over Mg-supported Al₂O₃ catalysts [8]. They found that the Mg/Al₂O₃ catalyst calcined at 650 °C has a higher amount of weak acid sites, an important factor for HFC-134a decomposition [8]. Song et al. tested CF₄ decomposition over metal-supported Al₂O₃ and elucidated that modification of the catalyst by metal impregnation preserves its active sites [10]. They found that using a metal-sulfate precursor could further enhance the catalytic performance by increasing the acid sites [10]. Takita et al. investigated metal sulfate catalysts for CCl₂F₂ decomposition [11]. The authors insisted that metal oxides were not stable for CCl₂F₂ decomposition, due to weak resistance to HF, while metal sulfate catalysts, especially Zr(SO₄)₂, achieved complete conversion over 350 °C in the presence of water vapor [11]. Previous research on the use of acid-treated catalysts for the decomposition of other fluorinated hydrocarbons suggest that the catalytic efficiency and stability of Al₂O₃-based catalysts can be increased by acid treatment, but there has been little systematic investigation on using alumina-based catalysts for HFC-134a decomposition [8,10–13].

In this study, Ga-Al₂O₃ and S/Ga-Al₂O₃ catalysts were prepared to investigate the change in the properties of the catalyst on acid treatment. Furthermore, the effect of the HF gas produced by HFC-134a decomposition on the catalyst was investigated.

2. Results and Discussion

2.1. Improvement in Catalytic Performance in HFC-134a Decomposition

Pristine Ga-Al₂O₃ and sulfuric acid-treated Ga-Al₂O₃ catalysts were synthesized and tested for HFC-134a decomposition reaction. To ensure the elemental composition of as-prepared catalysts, the amounts of Ga and Al were estimated by inductively coupled plasma, and that of S was measured by an elemental analyzer, given in Table 1. Figure 1 shows the temperature dependence of HFC-134a conversion over Ga-Al₂O₃ and S/Ga-Al₂O₃ catalysts. The catalysts exhibited markedly different performances. S/Ga-Al₂O₃, having a small amount of H₂SO₄ loading (1 wt.% of S), exhibited a higher HFC-134a conversion (90.5% at 450 °C) than Ga-Al₂O₃ (62% at 450 °C).

Table 1. Elemental composition of Ga-Al₂O₃ and S/Ga-Al₂O₃ catalysts.

Sample	Ga (wt.%) *	Al (wt.%) *	S (wt.%) **
Ga-Al ₂ O ₃	14.7	52.8	
S/Ga-Al ₂ O ₃	15.3	53.5	1.51

* Estimated by inductively coupled plasma—optical emission spectrometry. ** Estimated by elemental analyzer.

It has been reported that large amounts of HF molecules are inevitably produced during HFC-134a decomposition, which negatively affects the catalyst performance because of halogenide formation on the catalyst surface (Reaction (1)) [7]. In particular, the activity of the alumina-based catalyst is remarkably decreased by formation of AlF_3 (Reaction (2)) [7,14]. Thus, it is necessary to observe the catalyst stability during the HFC-134a decomposition reaction.

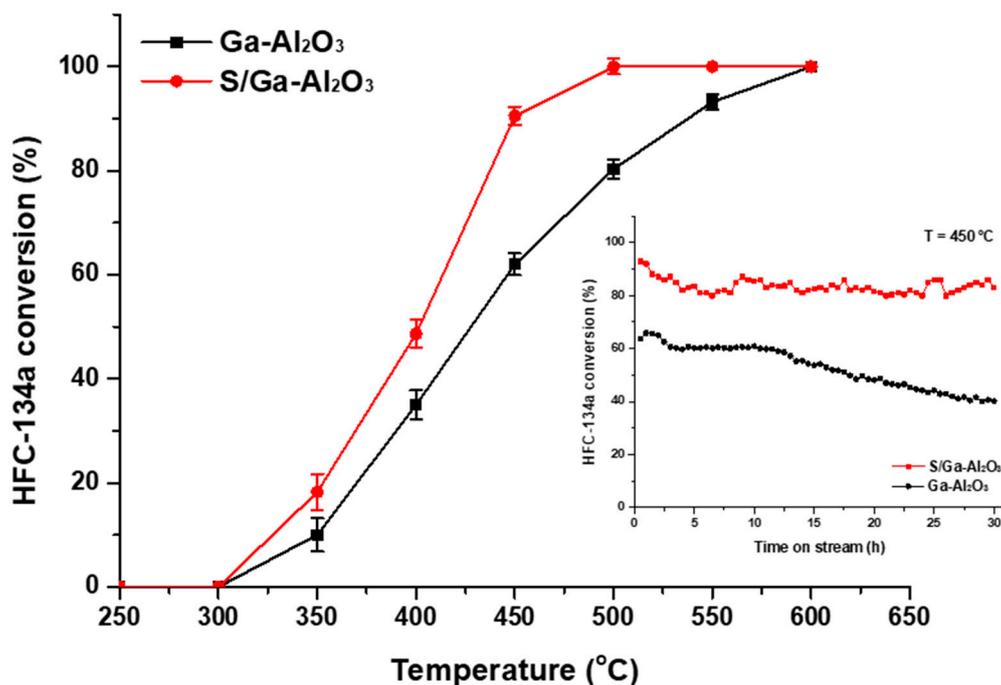
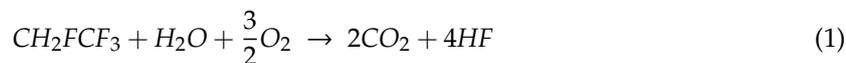


Figure 1. HFC-134a conversion over Ga-Al₂O₃ and S/Ga-Al₂O₃ catalysts. Reaction conditions: 1 vol.% HFC-134a, 25 vol.% H₂O in air balance; GHSV = 2362 h⁻¹. Inset: Catalytic stability test for the HFC-134a decomposition at 450 °C. Reaction condition: 1 vol.% HFC-134a, 25 vol.% H₂O in air balance; GHSV = 2362 h⁻¹.

The inset of Figure 1 presents the results of the catalyst stability test. It reveals that with time on stream, HFC-134a conversion over Ga-Al₂O₃ decreased much faster than that over S/Ga-Al₂O₃, retaining ~40% and 83% after 30 h, respectively. As both catalysts used the same amount of Ga (15 wt.%), it could be said that the large difference and good stability in HFC-134a decomposition performance are likely due to the pretreatment with sulfuric acid [14].

It has been reported that the catalytic properties such as crystallinity, surface area, and acidity are drastically influenced by pretreatment with sulfuric, hydrofluoric, nitric, and phosphoric acids [10,15,16]. XRD analysis was performed to confirm the crystal structure of our catalysts. Figure 2 presents the XRD patterns of Ga-Al₂O₃ and S/Ga-Al₂O₃ catalysts, revealing that both catalysts contained γ -Al₂O₃ (JCPDS #29-63) [17,18]. No peaks of Ga₂O₃ were observed in any case, which was ascribed to the high dispersion of Ga or the formation of Ga nanoparticles [17]. Therefore, only the γ -Al₂O₃ phase was detected by XRD [17,18]. The absence of sulfate-related peaks was attributed to the good dispersion of these species on the catalyst surface [19]. As shown in Table 2, Ga-Al₂O₃ and S/Ga-Al₂O₃ had BET surface areas of 227.5 and 187.4 m² g⁻¹ and total pore volumes of 0.35 and 0.29 m³ g⁻¹, respectively.

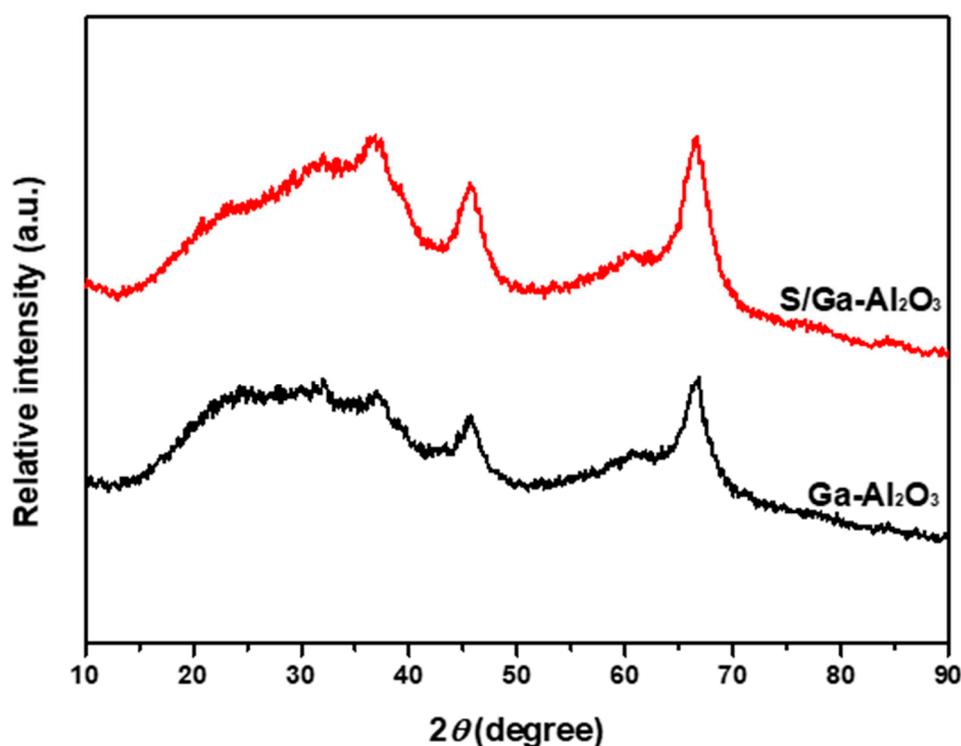


Figure 2. X-ray diffraction (XRD) patterns of fresh catalysts.

Table 2. Characterization results of catalysts: BET surface area, pore volume, and temperature-programmed desorption of ammonia (NH₃-TPD).

Samples	BET Surface Area [m ² g ⁻¹]	Pore Volume [m ³ g ⁻¹]	Amount of Acid Site [mmol g ⁻¹]			
			Weak	Medium	Strong	Total
Ga-Al ₂ O ₃	227.5	0.35	0.072	0.154	0.342	0.568
S/Ga-Al ₂ O ₃	187.4	0.29	0.117	0.207	0.312	0.646

When H₂SO₄ is doped in the mixed oxide, it generates acid sites on the catalyst [14,19]. Moreover, as sulfate ions are Lewis acids, they attract electrons to create new Lewis acid sites that could further improve the catalytic performance for HFC-134a decomposition [14,19]. Temperature-programmed desorption of ammonia (NH₃-TPD) and in situ FT-IR analysis were conducted to observe the acidic strength and type of surface acidity on Ga-Al₂O₃ and S/Ga-Al₂O₃ catalysts. Figure 3 presents the NH₃-TPD profiles of the two catalysts recorded at 55–700 °C. According to desorption temperature *T*, the sites could be grouped into those with weak (*T* < 250 °C), medium (250 °C < *T* < 400 °C), and strong (400 °C < *T*) acid sites, which implied the presence of sites with different acidic strengths [10,20]. Sulfuric acid treatment increased the amount of weak and medium acid sites, whereas that of strong acid sites was not significantly affected [21,22]. This finding indicates that the addition of sulfate strongly influences the acid properties of alumina-based catalysts [10,14,19]. The total amounts of acid sites of both catalysts are also listed in Table 2. The total acid sites were higher for S/Ga-Al₂O₃, indicating that sulfate addition increased the surface acidity.

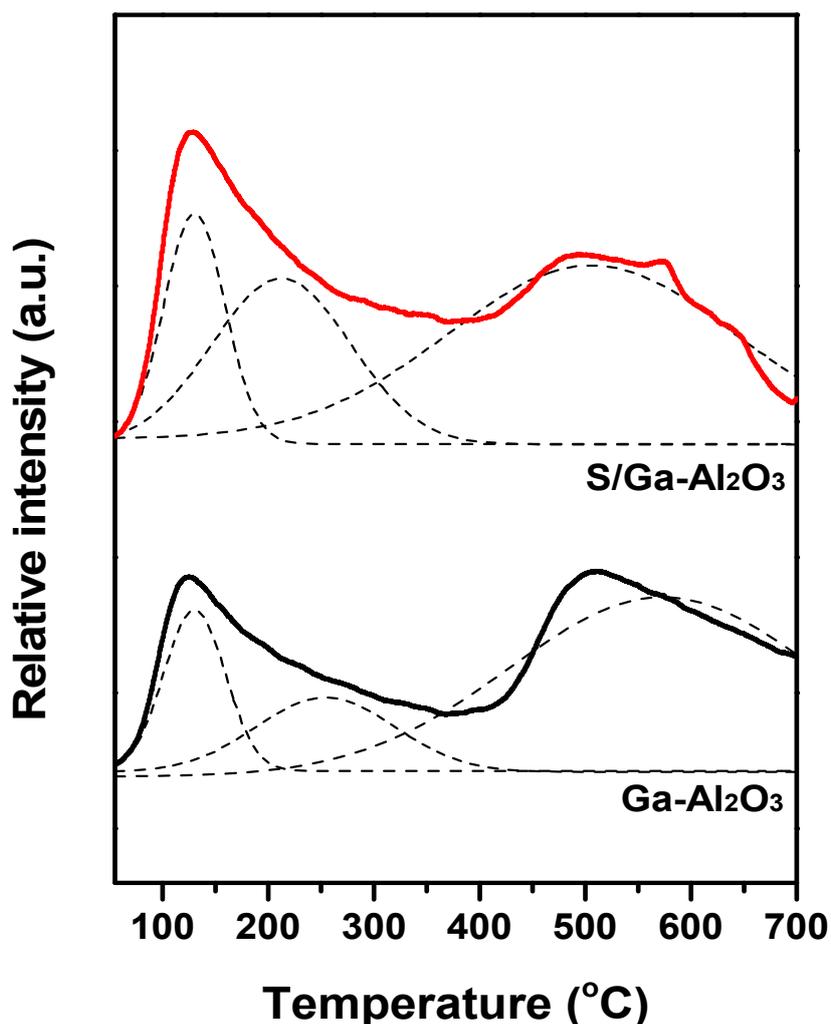


Figure 3. NH_3 -TPD following NH_3 adsorption in a flow of NH_3/He at $50\text{ }^\circ\text{C}$ for 1 h.

Figure 4 shows in situ FT-IR spectra of $\text{Ga-Al}_2\text{O}_3$ and $\text{S/Ga-Al}_2\text{O}_3$ catalysts exposed to a flow of NH_3 at $25\text{ }^\circ\text{C}$ for 1 h and then purged with He for 30 min to remove physically adsorbed species. In the case of $\text{Ga-Al}_2\text{O}_3$, peaks at 1262 , 1462 , 1612 , and 1689 cm^{-1} were detected, losing intensity with increasing temperature. The bands at 1262 and 1612 cm^{-1} corresponded to the bending vibrations of N–H bonds in coordinated NH_3^+ on Lewis acid sites, and the peaks at 1462 and 1689 cm^{-1} were attributable to NH_4^+ species on Lewis acid sites [14,19,23]. The spectra of $\text{S/Ga-Al}_2\text{O}_3$ were different from those of the $\text{Ga-Al}_2\text{O}_3$ catalyst, featuring adsorption bands at 1386 , 1486 , 1620 , and 1693 cm^{-1} . The band at 1620 cm^{-1} on $\text{S/Ga-Al}_2\text{O}_3$ was assigned to coordinated ammonia species, the same as 1612 cm^{-1} on the $\text{Ga-Al}_2\text{O}_3$ catalyst [14,19]. The bands at 1486 and 1693 cm^{-1} were due to NH_4^+ species on Lewis acid sites. These IR bands of NH_4^+ species (1486 and 1693 cm^{-1}) were blue-shifted by $\sim 20\text{ cm}^{-1}$ compared to those of the non-sulfated catalyst because of the higher NH_4^+ -catalyst bonding strength. Furthermore, a new peak at 1386 cm^{-1} in $\text{S/Ga-Al}_2\text{O}_3$ was observed at $250\text{ }^\circ\text{C}$, which was not detected below $200\text{ }^\circ\text{C}$, because of the nearby overlapping band. This could be assigned to the presence of medium Lewis acid sites, which are stable up to $500\text{ }^\circ\text{C}$. Thus, the NH_3 -TPD and FT-IR results imply that the amount of acid sites on the $\text{Ga-Al}_2\text{O}_3$ catalyst could be increased by sulfuric acid treatment.

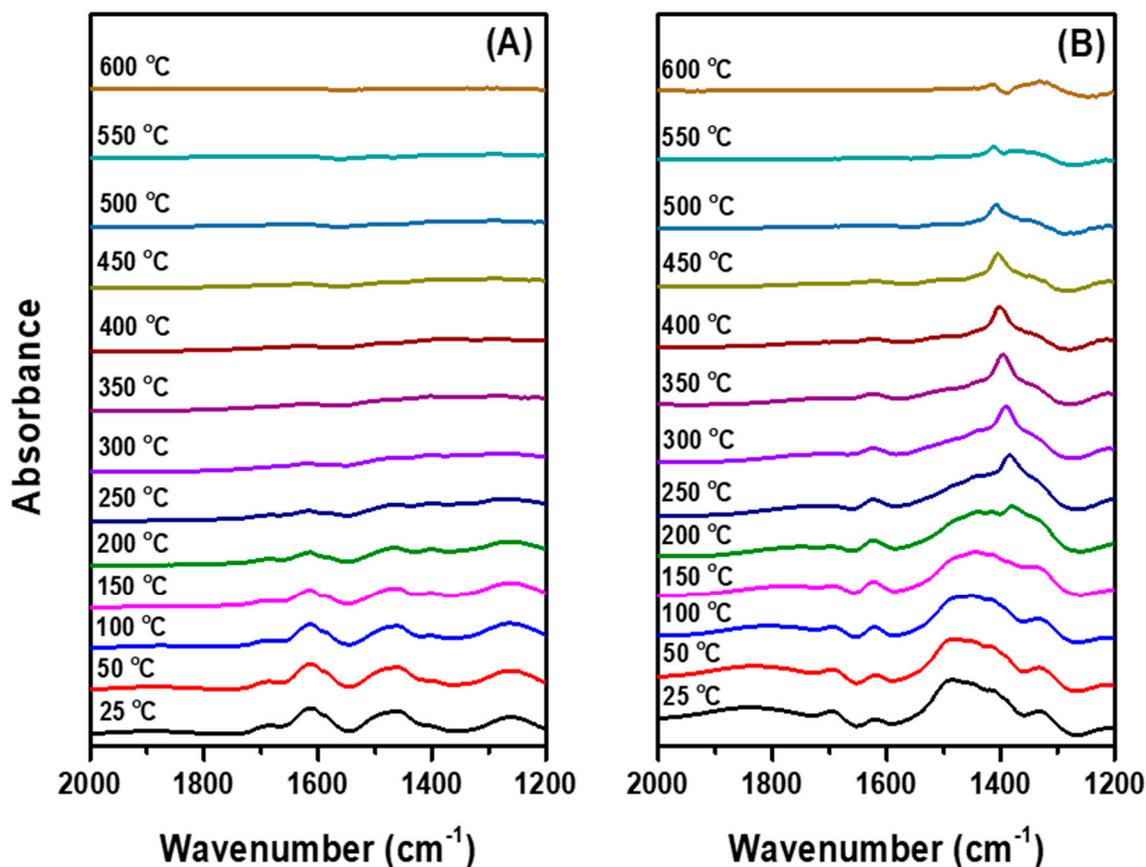


Figure 4. In situ FT-IR spectra as a function of temperature for fresh Ga-Al₂O₃ (A) and S/Ga-Al₂O₃ (B) catalysts in He flow after NH₃ adsorption.

Like the use of acid-treated catalysts for the decomposition of other fluorinated hydrocarbons, the catalytic activity for HFC-134a decomposition could be enhanced by acid treatment of the catalyst. Although sulfate treatment decreases the surface area and pore volume, it apparently increases the amount of Lewis acid sites that positively influence the HFC-134a decomposition.

2.2. Observation of Change in Surface Properties by HF Poisoning

As mentioned above, in the catalytic decomposition of HFC-134a, poisoning by HF is the main reason for catalytic deactivation. However, most of the studies so far have aimed only at improving the catalytic activity by increasing the acidity of the catalyst, and no detailed study of the physicochemical change on the used catalysts was investigated. We analyzed the change in the surface of the fresh and used catalysts via characterization by XRD, SEM-EDS, and XPS. For these analyses, the catalyst tested for 30 h in the HFC-134a decomposition reaction was referred to as a used catalyst.

The XRD pattern of used Ga-Al₂O₃ and S/Ga-Al₂O₃ catalysts is given in Figure 5. Used catalysts had γ -Al₂O₃ (JCPDS #29-63)-related peaks, and similar to the fresh catalysts, no peaks corresponding to Ga₂O₃ and sulfate species were detected [10,24]. However, the XRD patterns of used catalysts showed higher crystallinity than that of fresh catalysts, and characteristic peaks of AlF₃ were clearly detected for both used catalysts. Thus, it was qualitatively confirmed that regardless of the acid treatment, AlF₃ was formed on the catalyst surface during HFC-134a decomposition.

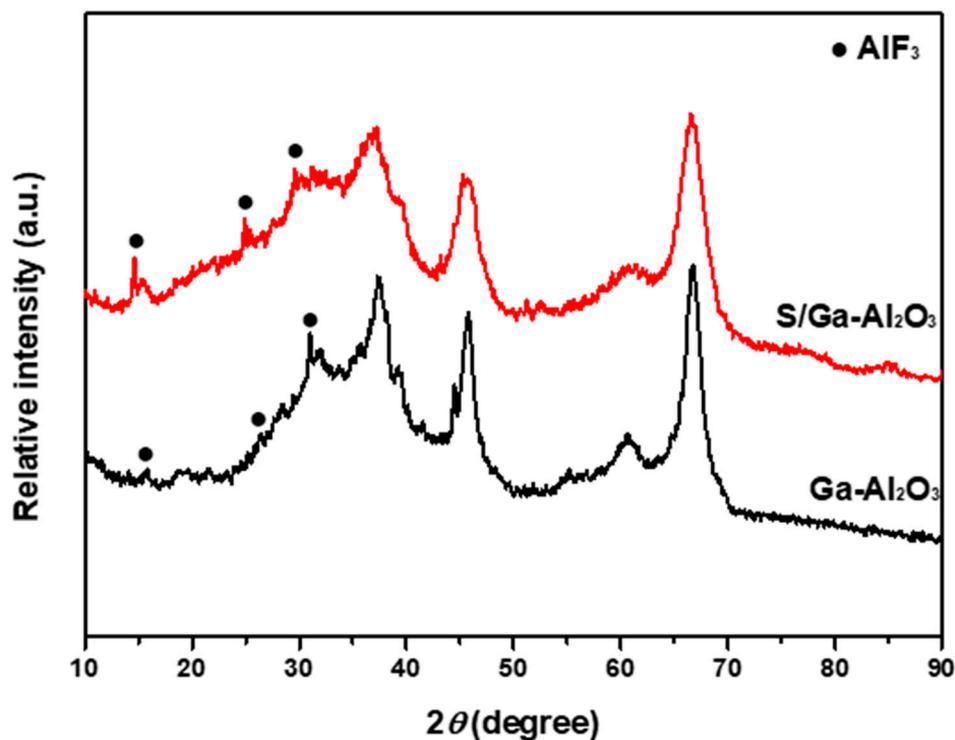


Figure 5. X-ray diffraction (XRD) patterns of used catalysts.

To investigate the formation of AlF_3 located on the catalyst surface, SEM-EDS analysis was conducted on the used catalysts. Figure 6 shows the SEM images of the used catalysts, revealing the presence of AlF_3 on both catalyst surfaces (in agreement with the XRD analysis in Figure 5). More AlF_3 was observed on the surface of $\text{Ga-Al}_2\text{O}_3$ than on the surface of $\text{S/Ga-Al}_2\text{O}_3$. Table 3 shows the elemental compositions as determined by EDS. Although both used catalysts had similar Ga content, $\text{Ga-Al}_2\text{O}_3$ contained almost twice as much F as $\text{S/Ga-Al}_2\text{O}_3$. Therefore, in good agreement with the stability test, it might be concluded that sulfuric acid treatment not only improves the catalytic performance but also inhibits the formation of AlF_3 on the catalyst surface.

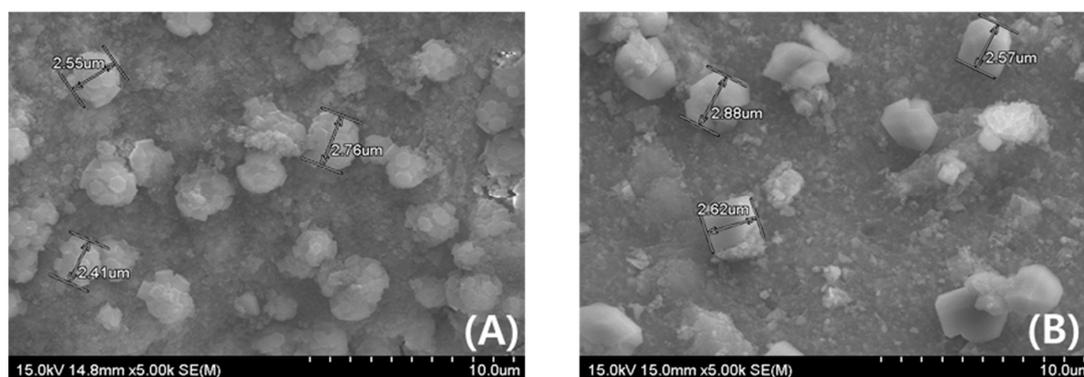


Figure 6. SEM images of used catalyst: $\text{Ga-Al}_2\text{O}_3$ (A), $\text{S/Ga-Al}_2\text{O}_3$ (B).

Table 3. EDS analysis of used catalysts.

Elements (Weight %)	Ga-Al ₂ O ₃	S/Ga-Al ₂ O ₃
Ga	13.9	13.8
Al	30.6	34.4
O	30.3	37.2
F	25.2	13.8
S		0.8

The surface electronic state and atomic concentration of Ga and Al in the fresh and used catalysts were investigated by XPS analysis. A curve-fitting for this analysis was carried out after Shirley-type background subtraction using a combination of Gaussian and Lorentzian functions. Figure 7A depicts the Ga 2p_{3/2} spectra for the fresh Ga-Al₂O₃ and S/Ga-Al₂O₃ catalysts. The XPS peaks of Ga 2p_{3/2} at 1117.4 and 1118.7 eV can be ascribed to Ga⁰ and Ga³⁺ [25–27]. The Ga⁰ peak increased with sulfuric acid treatment of the Ga-Al₂O₃ catalyst, indicating that the acid sites on the Ga-Al₂O₃ catalyst could partially reduce the Ga³⁺ to Ga⁰ because they attract electrons to create more Lewis acid sites. Figure 7B presents the Ga 2p_{3/2} spectra for the used Ga-Al₂O₃ and S/Ga-Al₂O₃ catalysts. There was little change in peak position compared to fresh catalysts. The Ga⁰/(Ga⁰ + Ga³⁺) values given in Table 4 are different for the used catalysts, because the HFC-134a decomposition occurs in a highly oxidative atmosphere and at high temperature. The Ga⁰/(Ga⁰ + Ga³⁺) value of the Ga-Al₂O₃ catalyst decreased from 0.30 to 0.11, while the S/Ga-Al₂O₃ catalyst retained Ga⁰ species after the HFC-134a decomposition reaction. This result clearly indicates that the sulfuric acid treatment not only increases the acidity of the catalyst but also increases and preserves partially reduced Ga⁰ species. The Al 2p spectra of the fresh catalysts are shown in Figure 7C. Both catalysts have a well-developed Al 2p peak located at 74.2 eV, indicating the formation of an Al-O bond [28,29]. The peak shift with Al 2p on sulfuric acid treatment was not observed. However, in Figure 7D, another set of peaks, attributed to the Al-F bond, appeared in the range of 76.6–75.9 eV for the used Ga-Al₂O₃ and S/Ga-Al₂O₃ catalysts [28]. According to the literature, the binding energy range of the Al-F bond was found at 75.6–76.6 eV [28]. The XPS results of Al in Figure 7D are very similar to that, which can be thought of as peaks due to the formation of Al-F bonding. In the case of the Ga-Al₂O₃ catalyst, moreover, the peak intensity of the Al-O bond is significantly decreased by the formation of the Al-F bond [28–30]. It indicates that the Al-F bond of AlF₃ was formed by the replacement of the Al-O bond of Al₂O₃ during the HFC-134a decomposition reaction. The appearance of the Al-F peak after the reaction indicates that F incorporation occurs only on the Al₂O₃ surface, and not Ga₂O₃. Furthermore, this result suggests that the sulfuric acid treatment on the Ga-Al₂O₃ catalyst could alleviate the elemental composition change from Al₂O₃ to AlF₃.

Table 4. Surface atomic concentration of Ga⁰/(Ga⁰ + Ga³⁺) and binding energies for the Ga⁰ and Ga³⁺ value in Ga 2p_{3/2}.

Samples	Ga ⁰ /(Ga ⁰ + Ga ³⁺)	Binding Energy (eV)	
		Ga ⁰	Ga ³⁺
Ga-Al ₂ O ₃	0.30	1117.4	1118.7
S/Ga-Al ₂ O ₃	0.44	1117.5	1118.8
Ga-Al ₂ O ₃ used	0.11	1117.5	1118.7
S/Ga-Al ₂ O ₃ used	0.41	1117.4	1118.8

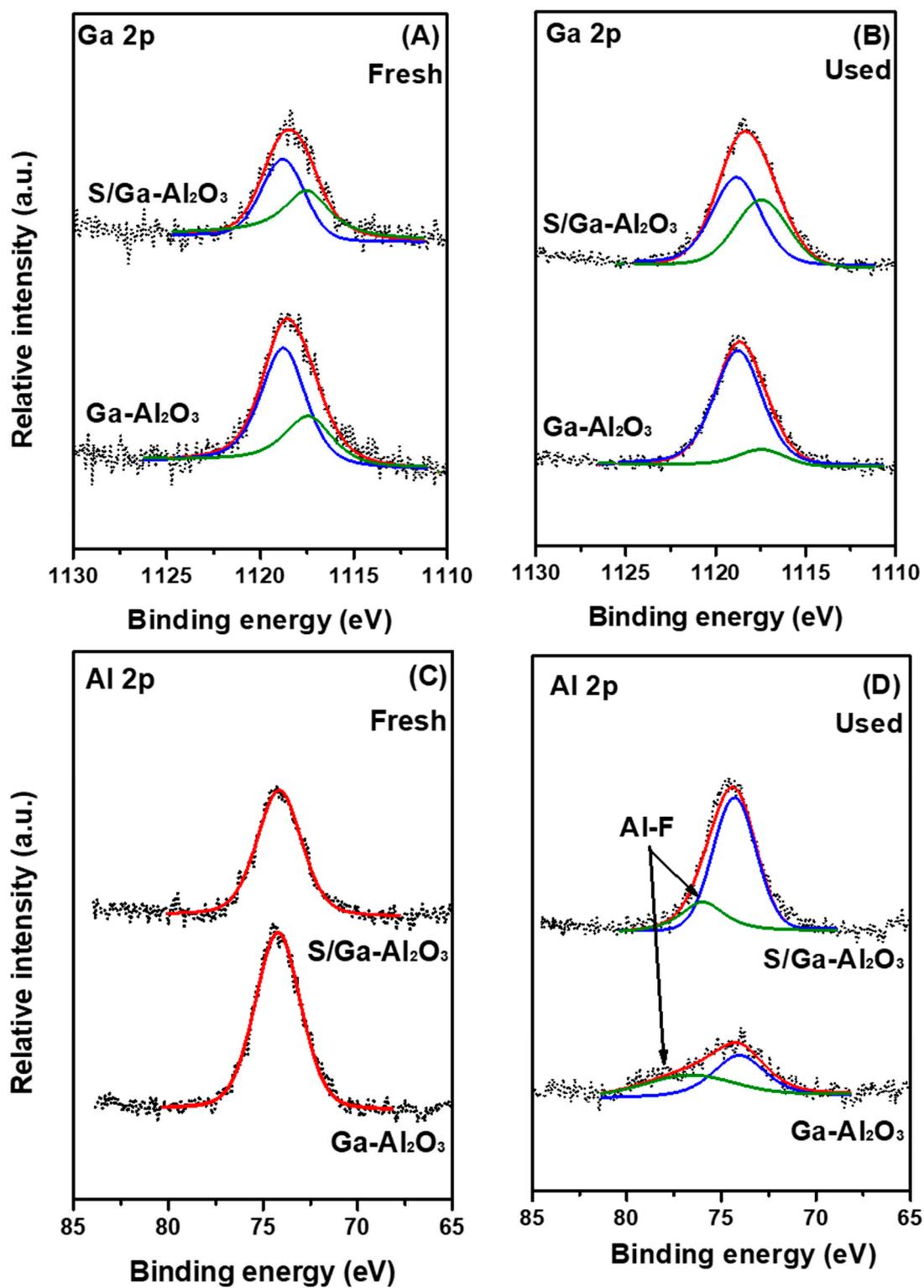


Figure 7. XPS spectra of Ga-Al₂O₃ and S/Ga-Al₂O₃ catalysts: (A) Ga 2p_{3/2} of fresh, (B) Ga 2p_{3/2} of used, (C) Al 2p of fresh, and (D) Al 2p of used.

3. Materials and Methods

3.1. Catalyst Preparation

Ga-Al₂O₃ was synthesized by co-precipitation, with the Ga loading fixed at 15 wt.%. Stoichiometric quantities of gallium nitrate (99.9%, Aldrich, St. Louis, MO, USA) and aluminum nitrate (98%, Aldrich) were dissolved in distilled water, and the resulting solution was slowly treated with 15 wt.% aqueous NH₄OH with vigorous agitation until the pH reached 9.1. The resulting slurry was aged for 24 h at room temperature, and the precipitate was thoroughly washed to remove impurities, dried at 110 °C for 24 h, and calcined at 600 °C for 5 h to finally obtain the Ga-Al₂O₃ catalyst. S/Ga-Al₂O₃ was prepared by impregnating the Ga-Al₂O₃ catalyst with appropriate amounts of H₂SO₄ (1 wt.% S) followed by drying at 110 °C for 24 h and calcination at 600 °C for 5 h.

3.2. Catalytic Reaction

The catalytic reaction was performed in a fixed-bed Inconel reactor (10.5 mm i.d.) under atmospheric pressure. The reaction temperature was determined by using a thermocouple directly inserted into the catalyst bed. Prior to the reaction, the catalyst powders were pressed into pellets, crushed, and sieved to 40–60 mesh. The reactant gas mixture (1 vol.% HFC-134a, 25 vol.% H₂O, and balance air) was introduced into the reactor at a gas hourly space velocity (GHSV) of 2362 h⁻¹. Water, quantitatively introduced using a syringe pump, was passed through a pre-heater at 200 °C before being injected into the reactor. To remove HF, the product gas was passed through aqueous KOH and then analyzed by an online gas chromatograph equipped with a thermal conductivity detector (iGC 7200, DS Science, Gwangju, Gyeonggi, R. Korea).

3.3. Characterization

The crystal structure of the catalyst was probed by X-ray diffraction (XRD, Rigaku D/MAX-2500, Cu K_α radiation). Brunauer–Emmett–Teller (BET) surface areas were determined from N₂ adsorption–desorption isotherms recorded at –196 °C (BELSORP-max, BEL Japan, Inc., Osaka, Japan). The structure of the catalyst samples was observed by scanning electron microscopy (SEM, Hitachi S-4300, Tokyo, Japan) coupled with energy-dispersive X-ray spectroscopy (EDS, Horiba EX-200, Horiba, Tokyo, Japan). Prior to the temperature-programmed desorption of ammonia (NH₃-TPD) experiments (BELCAT II, BEL Japan, Inc.), samples were pretreated in helium flow at 400 °C for 1 h to remove impurities, cooled to 50 °C, exposed to excess 5% NH₃/He for 1 h, and purged with He. NH₃-TPD was performed at temperatures of up to 700 °C in helium flow. In situ Fourier-transform infrared spectroscopy (FT-IR) was carried out in a ceramic IR cell equipped with ZnSe windows using a diffuse-reflectance infrared (IR) accessory (PIKE Technologies, Madison, WI, USA) connected to a Nicolet iS10 (Thermo Scientific, Waltham, MA, USA) IR spectrometer with an MCT-A detector. Spectra were recorded by the averaging of 64 scans with a resolution of 8 cm⁻¹. Before IR spectral observation, samples were pretreated in a flow of He at 400 °C for 1 h to remove impurities, and then cooled down to 25 °C to probe NH₃ adsorption behavior in the temperature range of 25–600 °C. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB Mark II spectrometer (Vacuum Generators, Su ssex, UK) using Al K_α radiation (*hν* = 1486.6 eV) at a constant energy of 50 eV. The binding energy was aligned based on the C 1s transition at 285 eV.

4. Conclusions

To investigate the effect of sulfuric acid treatment on catalysts for HFC-134a decomposition, Ga-Al₂O₃ and S/Ga-Al₂O₃ catalysts were prepared by co-precipitation and impregnation methods. The S/Ga-Al₂O₃ catalyst achieved a much higher HFC-134a conversion than Ga-Al₂O₃, which was ascribed to the promotional effects of sulfuric acid treatment on catalytic activity, as reported in many earlier studies for the catalytic decomposition of other fluorinated hydrocarbons. The effects of sulfuric acid treatment were probed by NH₃-TPD and in-situ FT-IR analysis. Treatment with sulfuric acid was shown

to influence the amount of Lewis acidity and improve the catalytic activity for HFC-134a decomposition. Furthermore, the S/Ga-Al₂O₃ catalyst retained its efficiency with minor fluctuation for the 30 h test, with its HFC-134a conversion maintained at ~80%.

The changes in surface structure of the used catalysts were characterized by XRD, SEM-EDS, and XPS analyses. Both catalysts contained AlF₃ after 30 h of HFC-134a decomposition reaction, confirmed by XRD. In particular, almost twice as many F sources were detected in the Ga-Al₂O₃ catalyst compared to the S/Ga-Al₂O₃ catalyst. Based on the XPS analysis results, the sulfuric acid treatment not only increased the acidity of the catalyst but also preserved the partially reduced Ga species. Moreover, this treatment could alleviate the elemental composition change from Al₂O₃ to AlF₃.

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Conflicts of Interest: The authors declare no conflict of interest.

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