





The Use of a γ -Al₂O₃ and MgO Mixture in the Catalytic Conversion of 1,1,1,2-Tetrafluoroethane (HFC-134a)

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Abstract: This paper reports the improved efficiency of 1,1,1,2-tetrafluoroethane (HFC-134a) decomposition by combined use of MgO with γ -Al₂O₃. While a high temperature (>900 °C) was required to achieve 90% conversion during non-catalytic pyrolysis of HFC-134a, 100% conversion of HFC-134a was achieved at 600 °C by the use of γ -Al₂O₃. Among the three catalysts (γ -Al₂O₃, MgO, and CaO) tested in this study, γ -Al₂O₃ showed the highest HFC-134a decomposition efficiency, followed by MgO and CaO, due to its large surface area and large amount of weak acid sites. Also with the longest lifetime among the catalysts, durability in maintaining complete decomposition of HFC-134a was shown in γ -Al₂O₃. The addition of MgO to γ -Al₂O₃ was effective in extending the lifetime of γ -Al₂O₃. Compared to the double bed γ -Al₂O₃-MgO configuration, the use of a mixed γ -Al₂O₃-MgO bed extended the catalyst lifetime more effectively.

Keywords: catalytic conversion; greenhouse gas reduction; HFC-134a; γ-Al₂O₃; MgO

1. Introduction

The anthropogenic impact on climate change has drawn global attention to the reduction of greenhouse gases (GHG). Different from the Kyoto Protocol (1997), which requires the reduction of GHG emission in developed countries, the Paris Agreement (2015) demands all nations of the world to devote decisive action to deeply cutting GHG emissions. Recently, the Paris rulebook was established in the 24st Conference of the Parties (COP24) of United Nations Framework Convention on Climate Change (UNFCCC) held in Katowice, Poland, demanding an increase in greenhouse gas reduction technologies.

Hydrofluorocarbons (HFCs) are one of the six major GHGs in the Kyoto Protocol. Since HFCs show high global warming potential (GWP), ranging from 124 to 14,800 [1], their reduction is considered to be cost-effective. In the EU, HFC emissions account for more than 90% in total fluorinated GHG emissions and have more than tripled since 1990 [2]. Not only in the EU, there will be similar trends in other countries. As HFCs were used since the 1990s, the end of life of the electric devices filled

with HFCs is coming and the emissions of HFCs are expected to increase dramatically. The Kigali Amendment promulgated the phase-down on production and consumption of HFCs [3]. It is urgent to develop efficient mitigation technologies for HFCs, along with seeking new generation refrigerants which have no adverse ozone depletion and climate change effects.

Extensive studies have been carried out on the destruction of HFCs, including combustion, plasma technologies and catalytic decomposition [4–7]. Thermal combustion and plasma technologies have been regarded as reliable destruction and removal processes for ozone-depleting substances like primary chlorofluorocarbons (CFCs) and halons. Despite their excellent destruction efficiency for HFCs, they consume large amounts of energy and can generate secondary air pollutants [4].

Catalytic conversion is considered as an alternative process in decomposing 1,1,1,2-tetrafluor oethane (HFC-134a), which is one of the major HFCs and used extensively as refrigerant. Catalytic conversion has advantages regarding low energy consumption, in that it can react at temperatures lower than 973K with alumina-based catalysts [7]. Also, a precious by-product is produced after catalytic conversion of HFC-134a. Trifluoroethylene (TrFE; CF₂=CHF; HFO-1123) is a major by-product during catalytic conversion of HFC-134a with Al_2O_3 . TrFE is a valuable material which can be utilized as a co-monomer or next generation refrigerant revealing a low global warming potential [8–11].

Up to now, alumina catalyst (Al₂O₃) in the gamma phase (γ) is known as an efficient catalyst for the decomposition of fluorinated gases. The performance of γ -Al₂O₃-based catalysts in the decomposition of HFCs [12] and PFCs [13] has been investigated in previous studies. Although the catalytic activity of γ -Al₂O₃ in the conversion of HFC-134a is high, only a few studies have been conducted on the deactivation mechanism of γ -Al₂O₃ and its enhancement method. The key points of catalytic conversion process are reaction efficiency, selectivity and the lifetime of catalysts. Previous studies were mainly focused on the reaction efficiencies.

Therefore, in this study, we compared the catalytic efficiencies of three selected catalysts (γ -Al₂O₃, MgO and CaO) and investigated key factors affecting the reaction efficiency based on measurements of specific surfaces area and the amount of acid sites. The deactivation mechanism of the catalysts was identified with long-term tests and surface characterization of spent catalysts after various reaction times using X-ray diffraction (XRD) and Energy Dispersive X-ray Spectrometry (EDS). Based on the identified deactivation mechanism, we attempted to improve the lifetime of the γ -Al₂O₃ catalyst by the addition of MgO in the catalyst bed for the decomposition of HFC-134a. This process is much more convenient, simple, and economically viable due to the low cost of MgO compared to that of γ -Al₂O₃. This application is beneficial in that the HF generated as a result of the dehydrofluorination reaction of HFC-134a can be neutralized by alkali metal oxides, impeding gas-solid reaction between HF and the γ -Al₂O₃ catalyst. This will prevent rapid deactivation of the main catalyst and, subsequently, extend the catalytic activity.

2. Results and Discussion

2.1. Thermal and Catalytic Decomposition of HFC-134a over Single Bed Catalyst

Figure 1 shows the effect of reaction temperature on the non-catalytic and catalytic conversion of HFC-134a over γ -Al₂O₃, MgO, and CaO. Owing to the thermal stability of HFC-134a [7], the thermal decomposition of HFC-134a was initiated at temperatures higher than 600 °C. The conversion efficiency of HFC-134a was gradually increased up to 89.9% by elevating the reaction temperature from 600 to 900 °C. Meanwhile, the catalytic conversion of HFC-134a over all catalysts was initiated even at the lowest temperature (300 °C) applied in this study. The conversion efficiencies of HFC-134a over all catalysts were increased by elevating the reaction temperature from 300 to 600 °C. Among the selected catalysts, γ -Al₂O₃ revealed the highest HFC-134a conversion efficiency at all temperatures, followed by MgO and CaO. At 600 °C, the catalytic conversion of HFC-134a over γ -Al₂O₃ achieved complete conversion and the conversion efficiencies of MgO and CaO were 92% and 64%, respectively.



Figure 1. Short-term conversion efficiencies of HFC-134a obtained from the non-catalytic and catalytic conversion of HFC-134a over γ -Al₂O₃, MgO, and CaO at different temperatures.

Figure 2 shows the time on stream HFC-134a conversion efficiencies over 12 h for γ -Al₂O₃, MgO, and CaO. Complete conversion of HFC-134a over γ -Al₂O₃ was maintained until 9 h of reaction, and the conversion efficiency gradually decreased to 88% after 12 h. Meanwhile, the conversion of HFC-134a over MgO was initially high, but rapidly decreased to 37% after 6 h of reaction. CaO revealed the lowest conversion efficiency, even at the initial reaction time, among the selected catalysts. It also showed a dramatic decrease of HFC-134a conversion efficiency compared to γ -Al₂O₃ and MgO. The conversion efficiency of HFC-134a over CaO rapidly decreased from 64% to 29% within 1 h and maintained a low HFC-134a conversion efficiency between 20 and 40% until the end of the test cycle (12 h). The above results indicate that the γ -Al₂O₃ displays not only higher conversion efficiency in the initial stage, but also longer lifetime during continuous reaction than those of other catalysts used in this study.



Figure 2. The changes of HFC-134a conversion efficiencies during continuous reaction of HFC-134a over γ -Al₂O₃, MgO, and CaO for 12 h at 600 °C.

can be explained by their respective specific surface areas and acidic properties. The BET surface area (S_{BET}) of γ -Al₂O₃, 187 m²/g, was higher than that of MgO (144 m²/g) and much greater than that of CaO (3 m²/g). The higher surface area of catalyst can allow more chances for contact between reactants, thus allowing better mass transfer conditions of the reactants [14,15]. Another important key factor affecting conversion efficiency of HFC-134a was the acidic property of the catalyst. Figure 3 and Table 1 show the temperature-programmed desorption of ammonia (NH₃-TPD) curves and the amount of weak, intermediate, and strong acid sites of fresh γ -Al₂O₃, MgO, and CaO, respectively. The amount of acid sites in the catalyst were classified to weak, intermediate, and strong acid sites based on the NH₃-desorption temperature region; weak at below 250 °C, intermediate at between 250 and 400 °C, and strong at above 400 °C [16].



Figure 3. NH₃-TPD curves of fresh catalysts used in this study.

Table 1. The amount of weak, intermediate, strong, and total acid sites of fresh γ -Al₂O₃, MgO, and CaO.

Catalyst -	Amount of Acid Sites (mmol-NH ₃ /g-Catalyst)						
	Weak	Intermediate	Strong	Total			
γ -Al ₂ O ₃	1.776	2.345	2.623	6.744			
MgO	0.614	0.753	0.397	1.764			
CaO	0.004	1.696	0.797	2.497			

Among the selected catalysts, γ -Al₂O₃ had the biggest amount of total acid sites, followed by CaO and MgO. This can explain the higher HFC-134a conversion efficiency of γ -Al₂O₃ than CaO and MgO. Although MgO had a smaller amount of total acid sites than CaO, its HFC-134a decomposition efficiency was higher than that of CaO owing to its much higher BET surface area. The higher performance of MgO than CaO can also be explained with the amount of weak acid sites. Although MgO had a lower amount of intermediate and strong acid sites than CaO, it had a much higher amount of weak acid sites than CaO. This suggests that the amount of weak acid sites on the catalyst is closely related with the decomposition efficiency of HFC-134a. Several researchers have also emphasized that the weak acid sites of the catalyst play a crucial role in the conversion of HFC-134a [12,13]. Jia et al. reported that the weak acid sites act as the reactive ones for HFC-134a decomposition, while strong acid sites

cause formation of coke from HFC-134a or TrFE [12]. The descending order of weak acid sites and S_{BET} of the catalysts, γ -Al₂O₃, MgO, and CaO, was in accordance with that of catalytic conversion efficiencies of HFC-134a, confirming that weak acid sites and S_{BET} play the important role on catalytic conversion of HFC-134a [13,17].

2.2. The Use of Al₂O₃ -MgO Catalysts on the Catalytic Decomposition of HFC-134a

The major by-products obtained from the catalytic decomposition of HFC-134a over γ -Al₂O₃ are known to be HF and TrFE [12]. Generated HF can react with γ -Al₂O₃ by gas-solid reaction forming AlF₃. Although AlF₃ can be a strong acid catalyst, it shows different catalytic activities depending on different phases. At temperatures over 600 °C, AlF₃ becomes an alpha (α) phase which does not exhibit any catalytic activity [18,19]. Since the reaction temperature in this study is 600 °C, γ -Al₂O₃ is deactivated when it is converted into AlF₃ during the HFC-134a conversion reaction. Therefore, the formation of AlF₃ during the catalytic conversion of HFC-134a needs to be minimized to extend the lifetime of γ -Al₂O₃ on the catalytic conversion of HFC-134a. Between CaO and MgO, MgO was chosen due to its greater amount of weak acid sites and larger BET surface area. Figure 4 shows the different conversion efficiencies of HFC-134a over single bed γ -Al₂O₃ (single Bed, SB), double bed γ -Al₂O₃-MgO (Double Bed, DB), and mixed bed γ -Al₂O₃-MgO (mixed single-bed, MD). Duration time maintaining the conversion efficiency of HFC-134a higher than 99% (DT99) over each catalyst bed were 4.4 h over SB- γ -Al₂O₃-1.2, respectively.



Figure 4. The changes of HFC-134a conversion efficiencies during long-term test over different catalyst beds for 12 h at 600 °C ($SB-\gamma-Al_2O_3-1.2$, single bed- $\gamma-Al_2O_3$ (1.2 g); DB- $\gamma-Al_2O_3-0.6$ -MgO-0.6, double bed- $\gamma-Al_2O_3$ (0.6 g) + MgO (0.6 g); MB- $\gamma-Al_2O_3-0.6$ -MgO-0.6, mixed bed- $\gamma-Al_2O_3$ (0.6 g) + MgO (0.6 g); SB- $\gamma-Al_2O_3-0.6$, single bed- $\gamma-Al_2O_3$ (0.6 g)).

Although it could not achieve higher and longer decomposition efficiency than SB- γ -Al₂O₃-1.2, DB- γ -Al₂O₃-0.6-MgO-0.6 revealed the longer DT₉₉ (6.9 h) than that of SB- γ -Al₂O₃-0.6. This suggests that the additional use of MgO can provide a higher conversion efficiency of HFC-134a, as can be expected with the result in Figure 2. When we compare SB- γ -Al₂O₃-1.2 and MB- γ -Al₂O₃-0.6-MgO-0.6, 0.6 g of MgO substituted 0.6 g of γ -Al₂O₃ with similar DT99. In case of SB- γ -Al₂O₃-0.6 and MB- γ -Al₂O₃-0.6-MgO-0.6, DT99 increased 1.6 times with addition of 0.6g MgO. Since the price

of γ -Al₂O₃ is much higher than that of MgO, additional use of MgO with γ -Al₂O₃ will highly reduce the cost of catalysts. Interestingly, MB- γ -Al₂O₃-0.6-MgO-0.6 led the longer DT₉₉ (8.8 h) than DB- γ -Al₂O₃-0.6-MgO-0.6 (6.9 h) on the decomposition of HFC-134a. This suggests that the lifetime of γ -Al₂O₃, MgO, or both of those catalysts can be extended by the use of mixed γ -Al₂O₃ and MgO.

The higher and longer catalytic activity of MB- γ -Al₂O₃-0.6-MgO-0.6 compared to DB- γ -Al₂O₃-0.6-MgO-0.6 can be explained by the synergistic effect on the conversion of HFC-134a enhanced by the different roles of γ -Al₂O₃ and MgO. During the thermal treatment of HFC-134a over γ -Al₂O₃, there are two reactions: (i) HFC-134a decomposition into HF and TrFE and (ii) γ -Al₂O₃ conversion to AlF₃ by gas-solid reaction with HF. When MgO was present together with γ -Al₂O₃, the HF preferred to react with MgO rather than γ -Al₂O₃ and MgO was converted to MgF₂. The HF consumption of MgO can prolong the lifetime of γ -Al₂O₃ and the dry mixing of γ -Al₂O₃, causing a synergistic effect which can increase the reaction efficiency and lifetime of the catalysts. A similar concept was proposed by Han et al. [20]. They achieved stable CF₄ conversion efficiency by the additional use of Ca(OH)₂ with γ -Al₂O₃ on the catalytic hydrolysis of CF₄ compared to the single γ -Al₂O₃.

The role of MgO was identified by the comparison XRD of spent catalysts in the presence or absence of MgO. In our result, the diffraction lines of fresh γ -Al₂O₃ and spent catalysts collected after the specific reaction times (6, 9, 12 h) were different. In the absence of MgO, γ -Al₂O₃ was converted into AlF₃ from the sample collected after the 6 h of reaction. This coincides with the decrease in catalytic conversion efficiency of HFC-134a over SB- γ -Al₂O₃-0.6 (Figure 5). The diffraction line corresponding to AlF₃ also increased with the increase of reaction time. This also confirms that the decrease of HFC-134a conversion efficiency is caused by the conversion of γ -Al₂O₃ to AlF₃. The formation of AlF₃ on the catalytic decomposition of HFC-134a is related with the gas-solid reaction of γ -Al₂O₃ with HF, which can be expressed as following Equation (1) [18]:



$$Al_2O_3 + 6HF \rightarrow 2AlF_3 + 3H_2O_1 \Delta_R G^0 = -329 \text{ kJ mol}^{-1}$$
 (1)

Figure 5. XRD results of fresh and spent γ -Al₂O₃ used in SB- γ -Al₂O₃-0.6.

Figure 6 shows the XRD results of fresh and spent catalysts used in DB- γ -Al₂O₃-0.6-MgO-0.6. In the case of DB- γ -Al₂O₃-0.6-MgO-0.6, γ -Al₂O₃ can be found until 9 h of reaction (Figure 6a) and MgO was gradually converted into MgF₂ (Figure 6b). As shown above, the HFC-134a conversion efficiency over DB- γ -Al₂O₃-0.6-MgO-0.6 started to decrease after 7 h and a 76% conversion efficiency was measured after 9 h. Combining the long-term test and XRD results, we can conclude that the conversion efficiency of HFC-134a is highly dependent on the presence of γ -Al₂O₃, and the addition of MgO extended the lifetime γ -Al₂O₃ by preventing fluorination of γ -Al₂O₃. Prevention of fluorination of γ -Al₂O₃ by MgO can also be found in the enthalpy change shown in Equation (2) below:



$$2AlF_3 + 3MgO \rightarrow Al_2O_3 + 3MgF_2, \ \Delta_R G^0 = -232 \ \text{kJ mol}^{-1}$$
 (2)



Figure 6. The XRD results of fresh and spent (a) γ-Al₂O₃ and (b) MgO used in DB-γ-Al₂O₃-0.6-MgO-0.6.

EDS was also conducted to identify the quantitative difference between SB- γ -Al₂O₃-0.6 and DB- γ -Al₂O₃-0.6-MgO-0.6. EDS result of fresh and spent γ -Al₂O₃ (Table 2) revealed that the contents of Al and O decreased together with the increase of the contents of F and C during long-term catalytic conversion of HFC-134a. The content of F greatly increased after 6 h and was maximized after 9 h due to the deactivation of γ -Al₂O₃ in the form of α -AlF₃ and the effective defluorination reaction and fixation of HF. After 12 h, the carbon content largely increased, meaning that the large amount of carbon coke is also formed after the deactivation of the catalyst (Figure S1).

Sample Conditions	γ -Al ₂ O ₃ (Element, wt%)				
Sample Conditions	Al	0	F	С	
Fresh	43.5	52.0	0	4.5	
After 6 h	21.1	26.7	36.1	16.1	
After 9 h	18.8	2.4	61.1	17.7	
After 12 h	10.3	1.5	40.8	47.4	

Table 2. EDS results for fresh and spent γ -Al₂O₃ used in the single-bed reactor.

Table 3 shows the EDS result for fresh and used γ -Al₂O₃ and MgO in a serial bed reactor. In contrast to the case of a single bed reactor, oxygen content in γ -Al₂O₃ was decreased more slowly. The noticeable increase of F and C was initiated after 9 h (Figure S1). This confirms that the deactivation by the accumulation of F and C to γ -Al₂O₃ was delayed by the additional use of MgO to γ -Al₂O₃.

Sample Conditions	γ -Al ₂ O ₃ (Element, wt%)			MgO (Element, wt%)				
	Al	0	F	С	Mg	0	F	С
Fresh	43.5	52.0	0	4.5	46.3	48.6	0	5.1
After 6 h	40.5	30.9	20.1	8.5	44.5	25.5	30.0	0
After 9 h	36.8	30.8	14.7	17.7	32.7	8.8	55.3	3.2
After 12 h	12.5	4.8	43.6	39.1	31.5	1.6	59.3	7.6

Table 3. EDS results for fresh and spent γ -Al₂O₃ and MgO used in the serial bed configuration.

According to the long-term conversion test of HFC-134a, XRD and EDS, it was found that the addition of MgO to γ -Al₂O₃ catalyst can be an efficient method for extending the catalyst lifetime in the catalytic conversion of HFC-134a. Deactivation of γ -Al₂O₃ was proceeded by fluorination at the first stage and by carbon deposition in the second stage. The lifetime of γ -Al₂O₃ was extended largely by the additional use of MgO on the catalytic decomposition of HFC-134a because of the slower fluorination of γ -Al₂O₃ with the help of the added MgO.

3. Experimental

3.1. Catalysts

 γ -Alumina (γ -Al₂O₃, Alfa Aesar, Haverhill, MA, USA), MgO (Daejung Chemicals and Metals Co., Ltd., Siheung, South Korea) and CaO (Junsei Chemicals Co., Ltd., Tokyo, Japan) were used as the catalysts for the catalytic decomposition of HFC-134a in this study. The catalysts were crushed, sieved to make their average particle size of 1.0–1.7 mm, calcined at 650 °C for four hours, and stored in a desiccator before use. In order to analyze the effect of each catalyst on the catalytic conversion of HFC-134a, 1.2 g of each catalyst was prepared as a single bed catalyst, respectively. To investigate the synergistic effect of different catalysts, double catalyst bed and mixed bed were prepared as shown in Figure 7. The double bed consisted of two catalyst layers, an upper bed with γ -Al₂O₃ (0.6 g) and a lower bed with MgO (0.6 g), and identified as "DB- γ -Al₂O₃-0.6-MgO-0.6". The mixed bed was prepared by dry mixing of 0.6 g of MgO and 0.6 g of γ -Al₂O₃. The catalyst performance of double bed and mixed bed were also evaluated by comparing their HFC-134a conversion efficiency with those of single γ -Al₂O₃ beds (0.6 or 1.2 g).





3.2. Catalytic Decomposition of HFC-134a Using a Lab Scale Fixed-Bed Reactor

The catalytic decomposition of HFC-134a was carried out in a lab-scale fixed-bed continuous reactor (Figure 8). The reactor system consisted of a reactor, syringe pump, mass flow controller, furnace, and HF trap. Reaction temperature was monitored using a thermocouple. 12 h of continuous reaction was conducted for each experiment. The reactor had 3.6 ml inner volume and was made with SUS-316L tube. Except for the case of 0.6 g γ -Al₂O₃ loaded single bed configuration, weight hourly space velocity (WHSV) was 5000 ml/g-catalyst while a mixture of input flow was composed of 2 mL/min of HFC-134a and 98 mL/min of nitrogen gas to make a total gas flow of 100 mL/min. Only the amount of γ -Al₂O₃ was reduced in the case of 0.6 γ -Al₂O₃ loaded single bed configuration. Flow rates of HFC-134a and nitrogen gas were controlled by mass flow controllers (MFCs) (Kofloc, Kojima Instruments Inc., Kyoto, Japan). The isothermal catalytic decomposition reaction was conducted at the temperature range of 300 °C up to 600 °C in 100 °C intervals. The produced HF was trapped by CaO pellet to reduce the HF amount in the effluent gas before entering the gas chromatograph (GC).



Figure 8. Schematic diagram of experimental setup for the catalytic decomposition of HFC-134a.

An online gas chromatograph (GC) (Agilent 7890A, Santa Clara, CA, USA) equipped with a GS-GASPRO column and a mass spectroscopy detector (MSD) (Agilent 5975C) was used. The composition of effluent gas was automatically analyzed every 15 minutes. NIST 8th library (National Institute of Standards and Technology, Gaithersburg, MD, USA, 2008) was used to identify each peak. MS peak areas of HFC-134a and main products were calculated in order to estimate relative amounts.

The conversion (%) of HFC-134a was calculated by comparing the MS peak area of HFC-134a in the reactant (before entering the reactor) and in the product gas (after the reaction). This calculation is expressed in Equation (3):

Conversion of HFC – 134a (%) =
$$\left(\frac{A_{in} - A_{out}}{Ain}\right) \times 100$$
 (3)

where, A_{in} and A_{out} are the MS peak areas of HFC-134a before entering the reactor and leaving the reactor, respectively. MS peak area of inflow (A_{in}) was determined using MS peak of HFC-134a in outflow at room temperature.

3.3. Characterizations

The specific surface area of the catalysts was measured via the BET equation using an Autosorb-iQ 2ST/MP apparatus (Quantachrome, Boynton Beach, FL, US). Before measurement, the samples were degassed at 300 °C for one hour. NH₃-TPD measurements to determine the acidic properties of the catalysts were conducted using a Micromeritics Autochem II 2920 analyzer (Norcross, GA, USA) equipped with a thermal conductivity detector (TCD). The sample (0.1 g) was heated at 100 °C for one hour under the He atmosphere at a flow of 50 mL/min and then cooled down to 50 °C. NH₃ adsorption was performed under a flow of 50 mL/min for one hour at 100 °C. Then, the physisorbed NH₃ was removed by flushing with He flow (50 mL/min) for one hour at 100 °C. Desorption of NH₃ was determined from 100 to 700 °C at a rate of 10 °C/min.

The changes in the crystallographic structure of fresh and used catalysts were examined by XRD using an Ultima IV system (Rigaku, Tokyo, Japan) over a 20 scan range of 10–80° operated at a voltage and current of 40 kV and 40 mA, respectively. Elemental analysis was carried out on a FESEM (S-4800, Hitachi, Tokyo, Japan) at accelerating voltage of 15 kV equipped with EDS to determine the element content of fresh and spent catalyst and absorbent. The content of coke deposition in the used catalysts was also measured by TGA analyzer (Pyris Diamond, Perkin Elmer, Waltham, MA, USA,). For this, the coke deposited catalysts (3 mg) were heated from room temperature to 800 °C under an air atmosphere (150 mL/min) at a heating rate of 10 °C/min.

4. Conclusions

The present study was designed to determine the factors affecting catalytic activity on the conversion of HFC-134a, to identify the deactivation mechanism of the catalysts, and to develop an economic conversion process by adding MgO in order to prevent fluorination of γ -Al₂O₃ catalyst. The effect of γ -Al₂O₃, MgO, CaO, and their mixture on the catalytic decomposition of HFC-134a was investigated using a lab scale fixed-bed reactor. Among the selected catalysts, γ -Al₂O₃ showed the highest conversion efficiency and longest lifetime during the long-term tests due to its larger surface area and greater amount of weak acid sites than MgO and CaO. The additional use of MgO together with γ -Al₂O₃ further increased the lifetime of γ -Al₂O₃ because the conversion of γ -Al₂O₃ to AlF₃ is delayed due to preferred reaction between HF and MgO. Compared to the double bed γ -Al₂O₃-MgO, mixed bed γ -Al₂O₃-MgO was more efficient in extending the catalyst lifetime and maintaining a high HFC-134a decomposition efficiency.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/11/901/s1, Figure S1. TG and DTG patterns of spent catalyst in (a) SB- γ -Al₂O₃-0.6 and (b) γ -Al₂O₃ and (c) MgO in DB- γ -Al₂O₃-0.6-MgO-0.6.

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