The Design of Sulfated Ce/HZSM-5 for Catalytic Decomposition of CF₄

Xie Zheng¹,², Shijie Chen¹,², Wanning Liu¹,², Kaisong Xiang²,³,* and Hui Liu¹,²

¹ School of Metallurgy and Environment, Central South University, Changsha 410083, China; zhengxie@csu.edu.cn (X.Z.); csj19940415@163.com (S.C.); liuwanning@csu.edu.cn (W.L.);
leolau@csu.edu.cn (H.L.)
² Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, Changsha 410083, China
³ School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China
* Correspondence: xiangkaisong@hotmail.com; Tel.: +86-731-88830875; Fax: +86-731-88710171

Abstract: CF₄ has a global warming potential of 6500 and possesses a lifetime of 50,000 years. In this study, we modified the HZSM-5 catalyst with Ce and sulfuric acid treatment. The S/Ce/HZSM-5 catalyst achieves 41% of CF₄ conversion at 500 °C, which is four times higher than that over Ce/HZSM-5, while the HZSM-5 exhibits no catalytic activity. The effects of modification were studied by using NH₃-TPD, FT-IR of pyridine adsorption, and XPS methods. The results indicated that the modification, especially the sulfuric acid treatment, strongly increased the Lewis acidic sites, strong acidic sites, and moderate acidic sites on catalysts, which are the main active centers for CF₄ decomposition. The mechanism of acidic sites increases by modification and CF₄ decomposition is clarified. The results of this work will help the development of more effective catalysts for CF₄ decomposition.

Keywords: CF₄; perfluorocompounds; catalytic decomposition; Lewis acid site; cerium; sulfuric acid treatment

1. Introduction

Perfluorocarbon (PFC) is a class of greenhouse-gas (GHG) in which all valences of carbon are satisfied with fluorine atoms [1,2]. CF₄ is considered as the most abundant and harmful in PFCs, and it has a high global warming potential, which is about 6500 times higher than that of CO₂ over a 100-year time scale [3]. Due to its symmetry and strong ionic character in the C–F covalent bond, which is the strongest bond (543 kJ mol⁻¹) in organic chemistry, the CF₄ molecule is extremely stable [4]. The aluminum production industry is considered as the main source of CF₄ emission. When the anode effect occurs in the electrolytic cell, the flux Na₃AlF₆ will react with the C anode to form CF₄ as in the equation below [5]. In 2018, the global CF₄ emission from aluminum production is 4.408 Gg, accounting for approximately 4% of total GHG emission in CO₂ equivalent [6]. However, the lifetime of CF₄ in atmosphere is 50,000 years while that of CO₂ is only 10–20 years. Therefore, it is necessary and important to remove CF₄ presented in the exhaust flue gas from the aluminum production industry.

4Na₃AlF₆ + 3C → 4Al + 12NaF + 3CF₄

To date, several methods have been developed for CF₄ abatement, such as fueled combustion, plasma, and catalytic hydrolytic decomposition [7–9]. Among them, the catalytic hydrolytic decomposition is considered as the ideal method for its high efficiency and mild reaction temperature compared to others.
HZSM-5 is a molecular sieve catalyst with Si, Al, and O elements as the framework, it has displayed excellent performance in chlorofluorocarbon and hydrofluorocarbon decomposition [10–13]. The catalytic behavior is related to its high specific surface area, strong acidity, and three-dimensional channel system. However, the amount of strong acidic sites and Lewis acidic sites are insufficient for CF$_4$ decomposition.

Cerium (Ce) is a good promoter for catalyst, due to its high oxygen-storage capacity, high oxygen-vacancy concentration, and the facile Ce$^{4+}$/Ce$^{3+}$ redox cycle, which enhances the electron transfer that generates more acidic sites [14,15]. For example, de Rivas et al. [12] studied the 1,2-dichloroethane decomposition over the Ce/HZSM-5 catalyst, and they achieved a 90% conversion that was attributed to the addition of Ce which increased the Lewis acidic sites. Chen et al. [16] synthesized a [Ce-(1,3,5-benzenetricarboxylic acid)]$(\text{H}_2\text{O})_6$ catalyst, and achieved a good activity for toluene oxidation with conversion of T$_{90\%}$ at 223 °C, the authors concluded that the catalytic activity was due to the great amount of acidic sites on catalyst. Moreover, some research suggests that the sulfuric acid treatment is an excellent strategy to significantly increase the Lewis acidic sites on catalysts, as the sulfate ions act as Lewis acidic sites; meanwhile, they attracted electrons to create more new acidic sites [17,18]. Song et al. [19] modified the $\gamma$-$\text{Al}_2\text{O}_3$ with Ce and sulfuric acid treatment for CF$_4$ catalytic decomposition, and found that the addition of Ce increased the acidic sites, the sulfuric acid treatment further enhanced the increase, and the CF$_4$ conversions were consistent with the amount of acidic sites. Although varied Lewis acid type catalysts can be applied in CF$_4$ decomposition, a high temperature (over 700 °C) is required to decompose the CF$_4$ molecule [20–22]. Therefore, we focused on developing a HZSM-5 based catalyst by modification with element Ce and sulfuric acid treatment for CF$_4$ decomposition below 700 °C.

Given the above reasons, a series of modified HZSM-5 catalysts were developed to hydrolytically decompose CF$_4$ at 500 °C. The aim of this work is to investigate the changes in the properties of the catalyst on the addition of Ce and acid treatment. The physicochemical properties of catalysts were characterized by different techniques. This study intended to elucidate the mechanisms of CF$_4$ decomposition over HZSM-5 based catalysts.

2. Experimental Section

2.1. Catalyst Preparation

The Ce/HZSM-5 catalyst was prepared using the impregnation–calcination method from the commercial molecular sieve HZSM-5 (Si/Al = 18, mole ratio, Nankai Univ, Tianjin, China) calcined at 650 °C in N$_2$ atmosphere for 5 h with an aqueous solution containing required amounts of cerium nitrate (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), followed by drying overnight at 80 °C. The Ce/HZSM-5 (10%Ce/HZSM-5) catalyst was crushed and sieved into 60–80 mesh. The Ce/HZSM-5 catalyst was impregnated with an aqueous solution containing H$_2$SO$_4$ (98%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) under stirring for 24 h and dry for 12 h at 60 °C, the impregnating solution was adjusted to yield the same SO$_4^{2-}$ (12 wt%) as S/Ce/HZSM-5, finally, calcined at 650 °C for 5 h in N$_2$ atmosphere. The S/Ce/HZSM-5 (12%S/10%Ce/HZSM-5) catalyst was crushed and sieved into 60–80 mesh.

2.2. Catalytic Activity Test

The hydrolytic decomposition of CF$_4$ was carried out in a fixed-bed reactor. The temperature was maintained at 500 °C. In the aluminum production, the CF$_4$ generated in electrolytic cell during the anode effect, the CF$_4$ concentration in the flue gas is about 1%. Therefore, the gas flow consists of 1% CF$_4$, 35% H$_2$O, and balanced by Ar. The water was pre-heated at 150 °C and then constantly introduced into the reaction system by using a syringe pump. The effluent gas was washed by aqueous potassium hydroxide to remove the produced HF, and then passed through a cold trap to remove water. Finally, the gas was analyzed by an online gas chromatography (GC-9790 II) equipped with a thermal conductivity detector (TCD).
2.3. **Catalyst Characterization**

The morphology of the samples was examined by scanning electron microscope (SEM, JSM-IT300LA, JEOL, Tokyo, Japan) with energy dispersive X-ray (EDX) analysis. The X-ray diffraction analysis was performed on a TTR III diffractometer (XRD, Rigaku, Tokyo, Japan). The chemical composition and state of the elements on catalyst surfaces were investigated by X-ray photoelectron spectroscopy (XPS, EscaLab 250Xi, Thermo Fisher, Waltham, MA, USA). The specific surface areas were measured with the N\textsubscript{2} adsorption method on an ASAP analyzer (BET, ASAP2020, Micromeritics, Norcross, GA, USA). Ammonia temperature programmed desorption (NH\textsubscript{3}-TPD, AutoChem II 2920, Micromeritics, Norcross, GA, USA) analyses were performed using the following procedures. A 100 mg sample was pretreated at 550 °C, with helium flow of 30 mL/min for 1 h, and then cooled to 50 °C. Ammonia (10% NH\textsubscript{3}/He) was introduced to the catalyst for 1 h at 50 °C. After that, the sample was flushed with helium of 50 mL/min for 1 h to remove absorbed NH\textsubscript{3}, then the temperature was programmed to increase to 900 °C at a rate of 10 °C/min. The amount of ammonia desorbed from the catalyst was detected using TCD. Fourier transform infrared spectra (FT-IR, Nicolet iS50, Thermo Fisher, Waltham, MA, USA) of pyridine absorption were conducted using the following procedures. The sample was pressed and put into an IR cell, and then it was degassed at 400 °C under vacuum for 2 h to dehydrate. Next, the cell was cooled to room temperature, and the background signal was recorded. After that, pyridine vapor was introduced to the system until reaching adsorption equilibrium. The sample was evacuated out at 150 °C for 30 min followed by cooling down to 50 °C, and then spectral acquisition was performed.

3. **Results and Discussion**

3.1. **Characterization of Catalysts**

The morphology and elemental distribution of catalysts were monitored by SEM and EDS mapping, as shown in Figure 1. The microscopic images of HZSM-5 (Figure 1A) exhibit the nano-blocky particles with a smooth surface. The modified catalyst Ce/HZSM-5 (Figure 1B) and the S/Ce/HZSM-5 (Figure 1C,D) exhibit rough surface, the catalysts were covered by small solid granule. The EDS mapping for S/Ce/HZSM-5 (Figure 1E–I) exhibits the uniform distribution of O, Si, Al, S and Ce, respectively.

The X-ray diffraction (XRD) was performed to investigate the crystal structure of the catalysts as in Figure 2. All the samples contain the HZSM-5 [23], and the peak of CeO\textsubscript{2} (JCPDS:34-0394) is observed in modified samples, indicating the formation of CeO\textsubscript{2} [24]. It should be noted that the peak of Ce\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} is not observed in the S/Ce/HZSM-5 catalyst, which indicated the absence of reaction between Ce and sulfuric acid during the catalyst preparation step. The specific surface area and pore diameter of catalysts were analyzed, as listed in Table 1. The surface area of catalysts decreased from 248 m\textsuperscript{2} g\textsuperscript{-1} to 148 m\textsuperscript{2} g\textsuperscript{-1}, and the pore diameter decreased from 2.38 nm to 2.28 nm after modified by Ce, these changes are in agreement with previous research [19,25], which may account for the formation of CeO\textsubscript{2} on the surface of catalysts, in addition to element Ce, some cation ions were replaced by Ce, the CeO\textsubscript{2} would block the original pore, results in the surface area and pore diameter decreasing. The surface area and pore diameter increased to 278 m\textsuperscript{2} g\textsuperscript{-1} and 2.28 nm, respectively, after the sulfate acid treatment. This may be due to the fact that acid treatment increased the amount of amorphous silica [26].
The addition of Ce decreased the amount of weak acidic sites, and pore diameter decreased. The surface area and pore diameter increased to 278 m$^2$ g$^{-1}$ and 2.63 nm, respectively, after the sulfate acid treatment. This may be due to the fact that acid treatment increased the amount of amorphous silica [26].

Kinetic studies were performed to analyze the catalytic activity of the catalysts. The catalytic activity of the catalysts was measured by monitoring the conversion of the反应物 to the产物. Table 1 shows the specific surface area and pore diameter for the catalysts.

**Table 1.** Specific surface area, pore diameter for the catalysts.

| Catalysts          | BET Surface Area (m$^2$ g$^{-1}$) | Pore Diameter (nm) |
|--------------------|-----------------------------------|--------------------|
| HZSM-5             | 248                               | 2.38               |
| Ce/HZSM-5          | 148                               | 2.28               |
| S/Ce/HZSM-5        | 278                               | 2.63               |

**Figure 1.** SEM of (A) HZSM-5, (B) Ce/HZSM-5, (C,D) S/Ce/HZSM-5, and SEM-EDS mapping for S/Ce/HZSM-5 (E-I).

**Figure 2.** X-ray diffraction (XRD) patterns of the catalysts, (1) HZSM-5, (2) Ce/HZSM-5, and (3) S/Ce/HZSM-5.

The XRD results are shown in Figure 2. All the samples contain the HZSM-5 structure, but the peak of CeO$_2$ is not observed in the S/Ce/HZSM-5 catalyst, which indicated the absence of reaction between Ce and sulfuric acid during the catalyst preparation step. The specific surface area and pore diameter of catalysts were analyzed, which indicated the absence of reaction between Ce and sulfuric acid during the catalyst preparation step.

TPD experiments were conducted to analyze the different kinds of acidic sites in the catalysts. There are three kinds of acidic site according to the desorption temperature of NH$_3$: weak acidic sites ($T_d < 600 ^\circ C$), moderate acidic sites ($600 ^\circ C < T_d < 850 ^\circ C$), and strong acidic sites ($T_d > 850 ^\circ C$). The TPD results are shown in Table 1.

Figure 2. X-ray diffraction (XRD) patterns of the catalysts, (1) HZSM-5, (2) Ce/HZSM-5, and (3) S/Ce/HZSM-5.
The NH₃-TPD experiments were conducted to analyze the different kinds of acidic sites in the catalysts. There are three kinds of acidic site according to the desorption temperature of NH₃ on catalysts: weak acidic sites (T < 250 °C), moderate acidic sites (250 °C < T < 600 °C), and strong acidic sites (T > 600 °C) [27–29]. The TPD results are shown in Figure 3 and Table 2, the HZSM-5 catalyst exhibited the most weak acidic sites (663 µmol g⁻¹) and the second highest amount of moderate acidic sites (267 µmol g⁻¹), the strong acidic site was not observed. The addition of Ce decreased the amount of weak acidic sites to 290 µmol g⁻¹ and increased the moderate acidic sites to 544 µmol g⁻¹, but still, no strong acidic site was observed. After further acid treatment, the amount of weak acidic sites decreased to 273 µmol g⁻¹ and the amount of moderate acidic sites increased to 855 µmol g⁻¹, the amount of strong acidic sites dramatically increased to 1274 µmol g⁻¹, which dominated over others. These findings strongly indicated that the impregnation with sulfate group influenced the acidic properties of catalysts, the amount of moderate and strong acidic sites significantly increased; moreover, the ratio of (strong + moderate)/weak was in the following order: S/Ce/HZSM-5(7.80) > Ce/HZSM-5(1.88) > HZSM-5(0.40).

![NH₃-TPD profiles of catalysts.](image)

**Table 2. NH₃-TPD acidic sites results for the catalyst.**

| Catalysts             | Weak | Moderate | Strong | Total | (Strong + Moderate)/Weak |
|-----------------------|------|----------|--------|-------|-------------------------|
| HZSM-5                | 663  | 267      | 0      | 930   | 0.40                    |
| Ce/HZSM-5             | 290  | 544      | 0      | 834   | 1.88                    |
| S/Ce/HZSM-5           | 273  | 855      | 1274   | 2402  | 7.80                    |

In order to gain more information on acidic properties of catalysts, the FT-IR spectra of pyridine adsorption experiments are conducted as shown in Figure 4 and Table 3. The spectra are recorded over a frequency range from 1400 cm⁻¹ to 1700 cm⁻¹, where characteristic vibration modes of adsorbed pyridine will appear. According to the references [30,31], the characteristic wave number of 1455 cm⁻¹, 1612 cm⁻¹ could be assigned to the pyridine species coordinatively adsorbed on Lewis acid sites, while the wave number of 1545 cm⁻¹, 1635 cm⁻¹ assigned to pyridinium ion formed on Bronsted acid sites, the 1490 peak was attributable to the L+B acid sites. The amounts of L-acid site on HZSM-5, Ce/HZSM-5 and
S/Ce/HZSM-5 were 120.57 µmol g⁻¹, 138.26 µmol g⁻¹ and 156.84 µmol g⁻¹, respectively. The amount of Brønsted acid sites showed the reversed trend, they were 233.91 µmol g⁻¹, 83.61 µmol g⁻¹ and 69.97 µmol g⁻¹, respectively. The ratio of Lewis/Brønsted was in the following order: S/Ce/HZSM-5(2.24) > Ce/HZSM-5(1.65) > HZSM-5(0.52). The results indicated that the addition of Ce increased the amount of Lewis acidic sites while decreasing the Bronsted acidic sites; furthermore, the acid treatment enhanced the influence.

| Catalysts       | Amount of Acid Site (µmol g⁻¹) | Lewis/Brønsted (L/B) |
|-----------------|--------------------------------|---------------------|
|                 | L-Acid Site                    | B-Acid Site         |                         |
| HZSM-5          | 120.57                         | 233.91              | 0.52                    |
| Ce/HZSM-5       | 138.26                         | 83.61               | 1.65                    |
| S/Ce/HZSM-5     | 156.84                         | 69.97               | 2.24                    |

3.2. Catalytic Performance of CF₄ Decomposition

The conversion reactions of CF₄ over catalysts were conducted at different temperature, as shown in Figure 5. The HZSM-5 exhibited no catalytic activity below 600 °C, and only 14% conversion of CF₄ while the temperature increased up to 700 °C. The Ce/HZSM-5 exhibited a higher CF₄ conversion compared to HZSM-5, the CF₄ conversions at 500 °C, 550 °C, 600 °C, 650 °C and 700 °C were 10%, 41%, 52%, 60% and 63%, respectively. As for the S/Ce/HZSM-5 catalyst, the CF₄ conversion was further enhanced, they were 41%, 50%, 63%, 66% and 67%, respectively. Moreover, at the temperature of 500 °C, the conversion of S/Ce/HZSM-5 was four times higher than that of Ce/HZSM-5. These results indicated that the acid treatment significantly increased the catalytic activity of Ce/HZSM-5, which showed a good agreement with the results of BET, NH₃-TPD and FT-IR.
The stability of catalysts was tested for 60 h at 500 °C as shown in Figure 6. The CF₄ conversion over S/Ce/HZSM-5 decreased from 41% to 34% (17% loss), while the conversion over Ce/HZSM-5 decreased from 11% to 7% (27% loss). The catalytic stability of S/Ce/HZSM-5 was much higher than that of Ce/HZSM-5. This may be due to the increment of acidic sites by acid treatment.

3.3. Mechanism Analysis of Hydrolytic Decomposition of CF₄

In order to demonstrate the main factor that promoted the catalytic activity of catalysts, the close correlation between CF₄ conversion and the ratio of (strong + moderate)/weak and Lewis/Brønsted were performed as shown in Figure 7. The correlation showed that the conversion is related to the ratio of (strong + moderate)/weak and the ratio of Lewis/Brønsted. Therefore, we concluded that the strong + moderate acidic sites and the Lewis acidic sites, are the main factor that promoted the activity of the catalysts. The HZSM-5 exhibited no catalytic activity due to its low ratio of (strong + moderate)/weak and Lewis/Brønsted.
Similarly, it has been reported that the Lewis acid sites and strong + moderate acid sites played a promoting role in the decomposition of hydrofluorocarbons [32–34]. The results strongly suggest that the direct participation of the acid sites in CF₄ decomposition is probably a step for subtracting fluorine atom from CF₄ molecule by Lewis acid sites. The addition of element Ce and the acid treatment could significantly influence the acidic property, resulting in increasing the catalytic activity and stability of catalysts in CF₄ decomposition.

Figure 7. Correlation between CF₄ conversion and ratio of (strong + moderate)/weak and Lewis/Brønsted.

In order to acquire insights into the surface chemical composition of catalysts, X-ray photoelectron spectroscopy (XPS) analysis of catalysts was carried out and shown in Figure 8 and Table 4. A curve-fitting for this analysis was carried out after Shirley-type background subtraction using a combination of Gaussian and Lorentzian functions. Figure 8A presented the S 2p core level spectra, the two major binding energy values were located at 168.90 eV and 170.10 eV, attributing to S 2p⁰ from SO₄²⁻. According to references [17,18,35], the S⁶⁺ from SO₄²⁻ could significantly increase the amount of Lewis acidic sites, which showed a good agreement with the results of NH₃-TPD and FT-IR. The O 1s core level spectra of catalysts were shown in Figure 8B, there are three major binding energy values located at range 528.9 to 529.5 eV, range 530.0 to 531.6 eV, and range 531.9 to 533.2 eV, attributing to O₃⁺, O₃²⁺, and O₄ads, respectively [36,37]. After the acid treatment, the peak of O₃lat disappeared, the intensity of peak for O₄ads increased, it could be concluded that the O₃lat were transformed to O₄ads, meanwhile, some of the O₃lat bonded with S⁶⁺ to form SO₄²⁻, then increased the amount of Lewis acidic sites. The Ce 3d core level spectra of catalysts are shown in Figure 8C, the peak v₂ (885.9 eV–886.3 eV) and peak u₂ (904.0 eV–904.5 eV) were ascribed to Ce³⁺, the peak v₃ (883.0 eV), peak v₄ (892.3 eV–897.1 eV), peak v₅ (898.8 eV), peak u₃ (905.9 eV–907.7 eV) and peak u₄ (917.5 eV) were ascribed to Ce⁴⁺ [38,39], after the sulfuric acid treatment, the peak u₃ and peak v₄ disappeared, the Ce³⁺/Ce increased from 25.9% to 31.0%, indicating that the sulfuric acid treatment reduced the Ce⁴⁺ to Ce³⁺ because they attracted electrons to create more Lewis acidic sites, which showed a good agreement with the CF₄ conversion performance and the results of NH₃-TPD and FT-IR.
4. Conclusions

We modified the commercial HZSM-5 with the addition of Ce(Ce/HZSM-5) and further sulfuric acid treatment (S/Ce/HZSM-5). The S/Ce/HZSM-5 catalyst achieved a 41% CF₄ conversion at 500 °C which is four times higher than that over Ce/HZSM-5, while the HZSM-5 exhibited no catalytic activity. The close correlation between CF₄ catalytic conversion and acidic property indicated that the Lewis acidic sites and moderate + strong acidic sites are the main factors that promoted the activity of the catalysts. The effects of modification were confirmed by using NH₃-TPD, FT-IR of pyridine adsorption and XPS methods. These results indicate that the acidity properties of catalysts are strongly influenced by the addition of Ce and further sulfuric acid treatment, and then significantly improved the catalytic activity in the CF₄ decomposition process, which is an acid-catalyzed reaction.

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**Table 4.** Surface atomic distribution of element O and Ce.

| Catalysts        | O$_{\text{lat}}$ (%) | O$_{\text{sur}}$ (%) | O$_{\text{ads}}$ (%) | Ce$^{3+}$/Ce |
|------------------|----------------------|----------------------|----------------------|--------------|
| HZSM-5           | 0                    | 0                    | 100                  | /            |
| Ce/HZSM-5        | 10.5                 | 22.0                 | 67.5                 | 25.9         |
| S/Ce/HZSM-5      | 0                    | 10.1                 | 89.9                 | 31.0         |

**Figure 8.** X-ray photo electron spectroscopy (XPS) spectra of catalyst. (A): S 2p for catalyst, (B): O 1s for catalysts, and (C): Ce 3d for catalysts. (1) HZSM-5, (2) Ce/HZSM-5, and (3) S/Ce/HZSM-5.
28. Benaliouche, F.; Boucheffa, Y.; Ayrault, P.; Mignard, S.; Magnoux, P. NH₃-TPD and FTIR spectroscopy of pyridine adsorption studies for characterization of Ag- and Cu-exchanged X zeolites. *Microporous Mesoporous Mater.* **2008**, *111*, 80–88. [CrossRef]

29. Luo, J.; Kamasamudram, K.; Currier, N.; Yezerets, A. NH₃-TPD methodology for quantifying hydrothermal aging of Cu/SSZ-13 SCR catalysts. *Chem. Eng. Sci.* **2018**, *190*, 60–67. [CrossRef]

30. Xu, X.; Jeon, J.Y.; Choi, M.H.; Kim, H.Y.; Choi, W.C.; Park, Y.K. The modification and stability of γ-Al₂O₃ based catalysts for hydrolytic decomposition of CF₄. *J. Mol. Catal. A Chem.* **2007**, *266*, 131–138. [CrossRef]

31. Damyanova, S.; Centeno, M.; Petrov, L.; Grange, P. Fourier transform infrared spectroscopic study of surface acidity by pyridine adsorption on Mo/ZrO₂–SiO₂(Al₂O₃) catalysts. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2001**, *57*, 2495–2501. [CrossRef]

32. Takita, Y.; Anabe, T., Ito, M.; Ogura, M.; Muraya, T.; Yasuda, S.; Nishiguchi, H.; Ishihara, T. Decomposition of CH₂PCF₃ (134a) over Metal Phosphate Catalysts. *Ind. Eng. Chem. Res.* **2002**, *41*, 2585–2590. [CrossRef]

33. Swamidoss, C.M.A.; Sheraz, M.; Anus, A.; Jeong, S.; Park, Y.-K.; Kim, Y.-M.; Kim, S. Effect of Mg/Al₂O₃ and Calcination Temperature on the Catalytic Decomposition of HFC-134a. *Catalysts* **2019**, *9*, 270. [CrossRef]

34. Takita, Y.; Moriyama, J.-I.; Nishiguchi, H.; Ishihara, T.; Hayano, F.; Nakajo, T. Decomposition of CCl₂F₂ over metal sulfate catalysts. *Catal. Today* **2004**, *88*, 103–109. [CrossRef]

35. Wang, T.; Liu, H.; Zhang, X.; Liu, J.; Zhang, Y.; Guo, Y.; Sun, B. Catalytic conversion of NO assisted by plasma over Mn-Ce/ZSM-5-multil-walled carbon nanotubes composites: Investigation of acidity, activity and stability of catalyst in the synergic system. *Appl. Surf. Sci.* **2018**, *457*, 187–199. [CrossRef]

36. Zhao, H.; Zhao, H.; Han, W.; Dong, F.; Tang, Z. Enhanced catalytic performance of Nb doping Ce supported on ordered mesoporous TiO₂-SiO₂ catalysts for catalytic elimination of 1,2-dichlorobenzene. *Mol. Catal.* **2019**, *479*, 110638. [CrossRef]

37. Liu, B.; Li, C.; Zhang, G.; Yao, X.; Chuang, S.S.C.; Li, Z. Oxygen Vacancy Promoting Dimethyl Carbonate Synthesis from CO₂ and Methanol over Zr-Doped CeO₂ Nanorods. *ACS Catal.* **2018**, *8*, 10446–10456. [CrossRef]

38. Zong, L.; Zhang, G.; Zhao, H.; Zhang, J.; Tang, Z. One pot synthesized CeO₂-WO₃-TiO₂ catalysts with enriched TiO₂ (001) facets for selective catalytic reduction of NO with NH₃ by evaporation-induced self-assembly method. *Chem. Eng. J.* **2018**, *354*, 295–303. [CrossRef]

39. Han, W.; Zhao, H.; Dong, F.; Tang, Z. Morphology-controlled synthesis of 3D, mesoporous, rosette-like CeCoOₓ catalysts by pyrolysis of Ce[Co(CN)₆] and application for the catalytic combustion of toluene. *Nanoscale* **2018**, *10*, 21307–21319. [CrossRef]