The Role of Nitrate on the Sol-Gel Spread Self-Combustion Process and Its Effect on the NH₃-SCR Activity of Magnetic Iron-Based Catalyst

Xing Ning ¹, Zhi-bo Xiong ¹,²,*, Bin Yang ¹,², Wei Lu ¹,² and Shui-mu Wu ¹,³

¹ School of Energy and Power Engineering, University of Shanghai for Science & Technology, Jungong Road #512, Shanghai 200093, China; nx_1210@126.com (X.N.); usst_yangbin@163.com (B.Y.); luweinora@163.com (W.L.); wsm8855@126.com (S.-m.W.)
² Shanghai Key Laboratory of Multiphase Flow and Heat Transfer in Power Engineering, University of Shanghai for Science & Technology, Jungong Road #512, Shanghai 200093, China
³ SPIC Powder Plant Operation Technology (Beijing) Co., Ltd., Future Technology City, Beijing 102209, China

* Correspondence: xzb412@usst.edu.cn

Received: 25 February 2020; Accepted: 6 March 2020; Published: 10 March 2020

Abstract: Sol-gel spread self-combustion is the burning of the complexing agent in dried gel and the oxidant. Meanwhile, high temperature takes place during the combustion process, which is harmful to the pore structure of the catalyst. The nitrate from metal nitrate precursors as an oxidant could participate in the spread of the self-combustion process. Therefore, the influence of nitrate from metal nitrate on the spread self-combustion of an iron–cerium–tungsten citric acid gel and its catalytic performance of NOₓ reduction were investigated by removing nitrate via the dissolution of washing co-precipitation with citric acid and re-introducing nitric acid into the former solution. It was found that the removal of nitrate contributes to enhancing the NH₃–SCR activity of the magnetic mixed oxide catalyst. The NOₓ reduction efficiency was close to 100% for Fe₈₅Ce₁₀W₅–CP–CA at 250 °C while the highest was only 80% for the others. The results of thermal analysis demonstrate that the spread self-combustion process of citric acid dried gel is enhanced by re-introducing nitric acid into the citric acid dissolved solution when compared with the removal of nitrate. In addition, the removal of nitrate helps in the formation of γ-Fe₂O₃ crystallite in the catalyst, refining the particle size of the catalyst and increasing its pore volume. The removal of nitrate also contributes to the formation of Lewis acid sites and Bronsted acid sites on the surface of the catalyst compared with the re-introduction of nitric acid. The in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) demonstrates that both Eley–Rideal (E–R) and Langmuir–Hinshelwood (L–H) mechanisms exist over Fe₈₅Ce₁₀W₅–CP–CA at 250 °C with E–R as its main mechanism.

Keywords: selective catalytic reduction of NOₓ; sol-gel; the spread self-combustion method; nitrate; magnetic γ-Fe₂O₃

1. Introduction

Nitrogen oxide (NOₓ) emitted from coal-fired power plants and automobile engines has a strong negative influence on the environment and human health [1–6]. Selective catalytic reduction of NOₓ with NH₃ (NH₃–SCR) is well known as the best available control technology (BACT) to reduce nitrogen oxides due to its high efficiency [7,8]. Meanwhile, there exists some drawbacks such as high cost, high-temperature conversion of SO₂ to SO₃, the toxicity, and volatility of vanadium species for the commercial vanadium-based catalyst [9–16]. Due to the non-toxicity, low cost, environment, and the outstanding redox ability between Fe³⁺ and Fe²⁺, a series of iron-based mixed oxide catalysts prepared through co-precipitation, sol-gel, and impregnation methods have been developed by many
However, the sol-gel spread self-combustion method, also called low-temperature combustion synthesis (LCS), which takes advantage of organics (citric acid, glucose, urea, and so on) as reactants and nitrates from metal nitrates as oxidants, has been widely used to obtain nano-particles, ultrafine powders, and metal oxide catalysts [21–26]. In our precious studies, a novel Fe–Ce–W mixed oxide catalyst synthesized via the citric acid sol-gel spread self-combustion method exhibited high catalytic activity of NO$_x$ reduction with high-dispersive γ-Fe$_2$O$_3$ crystallite formed in it [27]. However, a large amount of heat is released during the spread self-combustion of the citric acid dried gel, and brings about a high temperature that acts on the obtained composite oxide catalyst, which might destroy the physical structure of catalyst, thereby influencing its catalytic performance of NO$_x$ reduction even though the duration of high temperature is short. Previous research has demonstrated that the amount of complexing agent as the fuel participated in the spread self-combustion of the dried gel, and affected the rapid oxidation of Fe$^{II}$ to Fe$^{III}$ [28]. Meanwhile, the oxygen from the surrounding air as an oxidant showed an enhancement effect on the spread self-combustion process of dried gel, which affected the structure properties of the obtained powder [29]. The nitrate from metal nitrate precursors as another oxidant could also participate in the spread self-combustion of dried gel. Therefore, it is necessary to investigate the influence of nitrate on the spread self-combustion of dried gel, especially its effect on the NH$_3$–SCR activity over the above magnetic iron–cerium–tungsten mixed oxide catalyst.

Herein, in the present work, two kinds of magnetic iron–cerium–tungsten mixed oxide catalysts were synthesized via the spread self-combustion of citric acid gel by removing nitrate through the dissolution of washing co-precipitation with citric acid, and re-introducing nitric acid into the former citric acid dissolved solution, respectively. Thermo-gravimetric analysis (TG-DTG-DSC) was used to study the influence of nitrate on the combustion of citric acid gel. In addition, x-ray diffraction (XRD), N$_2$-adsorption–desorption, x-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (H$_2$-TPR), temperature-programmed desorption (NH$_3$-TPD), and scanning electron microscope (SEM) were eventually used to characterize the physical structural and chemical properties of the catalyst.

### 2. Results and Discussion

#### 2.1. NH$_3$–SCR Activity

As can be observed from Figure 1, magnetic Fe$_{85}$Ce$_{10}$W$_5$–CP–CA synthesized through the spread self-combustion of the citric acid dried gel without the nitrate from the metal nitrate precursors exhibited excellent catalytic performance of NO$_x$ reduction at 150~400 °C, and more than 90% of NO$_x$ reduction was achieved at 225~400 °C and over, under a gaseous hourly space velocity (GHSV) of 60,000/h. Meanwhile, the re-introduction of nitric acid into the citric acid dissolved solution decreased the NH$_3$–SCR activity of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA, and the enhancement of nitrate ions from 0.5 to 2.0 further decreased its catalytic performance. This demonstrates that the nitrate brought from the precursors of metal nitrate shows an inhibition on the NH$_3$–SCR activity of the magnetic Fe$_{85}$Ce$_{10}$W$_5$ catalyst prepared through the spread self-combustion of citric acid gel. As shown in Table 1, the NO$_x$ conversion over per gram of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA at low temperature (125~200 °C) in one hour was still higher than those of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$), although the bulk density of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA was 0.7124 g/mL, which was higher than that of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$). Apparently, the re-introduction of nitric acid could participate in the spread self-combustion of citric acid dried gel, thereby decreasing the bulk density of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA. Therefore, the nitrate brought from the metal nitrate precursors shows an important role in the spread self-combustion of citric acid gel, thus affecting the physical structure and the redox properties of magnetic iron–cerium–tungsten mixed oxide catalyst. Herein, TG-DTG-DSC was used to investigate the combustion of the critic acid dried gels of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA and Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$).
The main burning temperature of dried gel compared with that of Fe\textsubscript{85}Ce\textsubscript{10}W\textsubscript{5} shows two steps weight loss of nitrate. Meanwhile, there exists an exothermic peak at 110–160 °C, and this also enhances the main burning temperature of dried gel compared with that of Fe\textsubscript{85}Ce\textsubscript{10}W\textsubscript{5} with a major mass loss about 37% at 160–220 °C. Therefore, the presence of NO\textsubscript{3}\textsuperscript{−} helps with the burning or/and decomposing of the citric acid dried gel [30]. Finally, the exothermic peak at 240–350 °C with a smaller weight loss could be considered as the gradual decomposition of citrates (ferric citrate, etc.) for these two dried gels.

2.2. Thermo-Gravimetric Analysis (TG-DTG-DSC)

Thermal analysis was carried out to investigate the relationship between the weight loss of the catalyst and temperature. The thermo-gravimetric (TG), differential thermo-gravimetric (DTG), and differential scanning calorimetry (DSC) traces of the Fe\textsubscript{85}Ce\textsubscript{10}W\textsubscript{5}–CP–CA and Fe\textsubscript{85}Ce\textsubscript{10}W\textsubscript{5}–CP–CA(NA\textsubscript{1.0}) citric acid gels were tested and the results are shown in Figure 2. The gel of Fe\textsubscript{85}Ce\textsubscript{10}W\textsubscript{5}–CP–CA(NA\textsubscript{1.0}) illustrates about 20% weight loss before approximately 140 °C, and a larger exothermic peak can be clearly observed from its DSC, which is mainly attributed to the decomposition of nitrate. However, the gel of Fe\textsubscript{85}Ce\textsubscript{10}W\textsubscript{5}–CP–CA shows two steps weight loss compared to the three steps weight loss of Fe\textsubscript{85}Ce\textsubscript{10}W\textsubscript{5}–CP–CA(NA\textsubscript{1.0}) gel. During the ignition, the gel of Fe\textsubscript{85}Ce\textsubscript{10}W\textsubscript{5}–CP–CA(NA\textsubscript{1.0}) presents a sharply spread self-combustion at about 140 °C with a large quantity of reddish brown gas released due to the decomposition of nitrate. Meanwhile, there exists an exothermic peak at 110–160 °C for Fe\textsubscript{85}Ce\textsubscript{10}W\textsubscript{5}–CP–CA(NA\textsubscript{1.0}) gel, or not an endothermic peak. This indicates that there exists a certain burning of citric acid at 110–160 °C, and this also enhances the main burning temperature of dried gel compared with that of Fe\textsubscript{85}Ce\textsubscript{10}W\textsubscript{5}–CP–CA with a major mass loss about 37% at 160–220 °C. Therefore, the presence of NO\textsubscript{3}\textsuperscript{−} helps with the burning or/and decomposing of the citric acid dried gel [30]. Finally, the exothermic peak at 240–350 °C with a smaller weight loss could be considered as the gradual decomposition of citrates (ferric citrate, etc.) for these two gels.
dried gels. Meanwhile, the decomposition temperature of the gradual citrates for Fe$_{85}$Ce$_{10}$W$_5$–CP–CA is lower than those of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$). Thus, it can be concluded that the existence of nitrate could enhance the spread self-combustion of citric acid gel, which affects the physical structure and redox properties of magnetic iron–cerium–tungsten mixed oxide catalyst, thereby influencing its low-temperature NH$_3$–SCR activity.

![Thermal analysis curves](image)

**Figure 2.** Thermal analysis curves of the precursor mixtures of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA and Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$) recorded under an air atmosphere. (A) thermo-gravimetric (TG), (B) differential thermo-gravimetric (DTG), and (C) differential scanning calorimetry (DSC).

2.3. Structural Properties

2.3.1. X-Ray Diffraction

The X-ray diffraction patterns of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA and Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$) were measured and the results are shown in Figure 3. It can be noted that there exists some obvious sharp diffraction peaks at 2θ = 30.2°, 35.6°, 43.3°, 53.7°, 57.4°, 62.7° in the samples, which are attributed to γ-Fe$_2$O$_3$ crystallite (#25-1402), and the diffraction peak at 2θ = 28.9° could be assigned to CeO$_2$ crystallite (#43-1002), according to the Joint Committee on Powder Diffraction Standards (JCPDS). This indicates that γ-Fe$_2$O$_3$ and CeO$_2$ are the main crystallites of magnetic Fe–Ce–W mixed oxide catalysts [19,31]. Meanwhile, the intensity of diffraction peaks attributed to the γ-Fe$_2$O$_3$ crystallite in Fe$_{85}$Ce$_{10}$W$_5$–CP–CA is stronger than that of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$). Therefore, the removal of nitrate promotes the formation of γ-Fe$_2$O$_3$ crystallite, which is usually thought to be an important active specie for NH$_3$–SCR reaction [27]. The re-introduction of nitrate also weakens the crystallization of CeO$_2$ in Fe$_{85}$Ce$_{10}$W$_5$–CP–CA. Meanwhile, the average γ-Fe$_2$O$_3$ crystallite sizes of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA...
and Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$) as calculated according to the Scherrer equation were 13.0 and 14.4 nm, respectively. Therefore, the re-introduction of nitrate causes a large amount of combustion heat to be released and results in a high temperature, thereby enlarging the particle size of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA. Then, the removal of nitrate helps in the formation of dispersive γ-Fe$_2$O$_3$ crystallites during the spread self-combustion of citric acid gel and restrains the inter-particle agglomeration and growth of the magnetic iron–cerium–tungsten mixed oxide catalyst.

![X-ray diffraction (XRD) spectra of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA and Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$).](image)

**Figure 3.** The x-ray diffraction (XRD) spectra of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA and Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$). (★ gama-Fe$_2$O$_3$ 25-1402, ▽ CeO$_2$ 43-1002).

2.3.2. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a useful technique to study the surface morphology, shape, and macroscopic particle size of the catalyst. Typical SEM pictures of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA, Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$), and their precursors before being ignited are shown in Figure 4. As shown in Figure 4A,B, the precursor of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$) shows stronger agglomeration than that of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA, and the combustion of dried gel at the presence of nitrate contributes to the agglomeration of the particles, and results in poor pore connectivity of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$), thus decreasing its pore volume. The particles in Fe$_{85}$Ce$_{10}$W$_5$–CP–CA have an outstanding distribution, contributing to the smaller pores and larger pore volume, which is beneficial to mass transfer and diffusion. Meanwhile, the diffusion of reactant gases and product gases among the pores of catalysts is important for NH$_3$–SCR reaction [31–33]. In addition, the removal of nitrate also decreases the particles’ average diameter of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA as calculated from the SEM in Figure 4C,D, which is in accordance with the particle sizes calculated according to the Scherrer equation.
The porosity and the pore size distribution of the as-prepared two catalysts were determined using N\textsubscript{2} adsorption–desorption. Figure 5 displays the N\textsubscript{2} adsorption–desorption isotherms, the pore size distributions of Fe\textsubscript{85}Ce\textsubscript{10}W\textsubscript{5}–CP–CA and Fe\textsubscript{85}Ce\textsubscript{10}W\textsubscript{5}–CP–CA(NA\textsubscript{1.0}), and their NO\textsubscript{x} conversions over per surface area in one hour (mg/(m\textsuperscript{2}·h)). As can be observed, the isotherm of Fe\textsubscript{85}Ce\textsubscript{10}W\textsubscript{5}–CP–CA(NA\textsubscript{1.0}) can be recognized as a type IV N\textsubscript{2} adsorption/desorption isotherm according to the International Union of Pure and Applied Chemistry (IUPAC) classification, and it presents mainly meso-pores (2–50 nm), however, the hysteresis loops of Fe85Ce10W5–CP–CA(NA1.0) and Fe85Ce10W5–CP–CA are the H2 and H1 type [32,34], respectively. This demonstrates that the removal of nitrate promotes the formation of meso-pores in magnetic, and the Fe85Ce10W5–CP–CA catalyst shows uniform and regular meso-pores, which was confirmed by the results of the pore diameter distribution in Figure 5B [35]. Interesting, the Brunauer-Emmett and Teller (BET) surface area of Fe85Ce10W5–CP–CA was 90.85 m\textsuperscript{2}/g, a little smaller than that of Fe85Ce10W5–CP–CA(NA1.0) (93.13 m\textsuperscript{2}/g), as shown in Table 2. Usually, a large BET surface area is beneficial to enhance the catalytic ability of the catalyst. Thus, the NO\textsubscript{x} conversions at low-temperature over per surface area of catalysts in one
hour were calculated, and it was found that Fe$_{85}$Ce$_{10}$W$_5$–CP–CA showed a higher NO$_x$ conversion over per surface area in one hour than Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$) at 150–200 °C.

![Figure 5. N$_2$ adsorption and desorption isotherms (A), pore diameter distributions (B), and desorption cumulative pore volume (C) of catalysts.](image)

**Table 2.** The surface area, pore volume, diameter, and average crystallite size of the catalysts.

| Samples               | $S_{\text{BET}}$ $^a$ (m$^2$/g) | Pore Volume $^b$ (cm$^3$/g) | Pore Diameter $^c$ (nm) | D $^d$ (nm) |
|-----------------------|----------------------------------|-----------------------------|--------------------------|-------------|
| Fe$_{85}$Ce$_{10}$W$_5$–CP–CA | 90.850                          | 0.178                       | 6.170                    | 13.000      |
| Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$) | 93.130                          | 0.146                       | 4.920                    | 14.400      |

$^a$ Brunauer-Emmett and Teller (BET) surface area; $^b$ Barrett-Joyner and Halenda (BJH) desorption pore volume; $^c$ Brunauer-Joyner and Halenda (BJH) desorption pore diameter; $^d$ Calculated according to the Scherrer equation.

2.3.4. X-ray Photoelectron Spectroscopy (XPS) and H$_2$-Temperature Program Reduction (H$_2$–TPR)

To investigate the influence of nitrate on the elements’ concentrations and chemical states on the surface of the catalyst, the XPS spectra of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA and Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$) were carried out. As can be noted from Table 3, the re-introduction of nitrate decreased the concentrations of cerium and tungsten on the surface of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA, and increased its surface concentration of iron. Higher surface Ce concentration contributes to the excellent reduction ability, which is widely known to be conducive for NH$_3$–SCR reaction [36]. To further study the influence of nitrate on the redox properties of the magnetic Fe–Ce–W mixed oxides catalyst, the H$_2$–TPR curves of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA and Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$) were obtained. The results in Figure 6 show that there exists one peak at the temperature range of 300–500 °C for these two samples, attributed to the reduction
from Fe$_2$O$_3$ to Fe$_3$O$_4$ at the range of 300~400 °C and the further reduction of Fe$_3$O$_4$ to FeO at about 500 °C [37–39]. Interestingly, the re-introduction of nitrate enhanced the low-temperature reducibility of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA by increasing its surface concentration of iron species, which is confirmed by the results of XPS in Figure 5. Meanwhile, the re-introduction of nitrate decreased the NH$_3$–SCR activity of the magnetic Fe$_{85}$Ce$_{10}$W$_5$–CP–CA catalyst.

Table 3. The X-ray photoelectron spectroscopy (XPS) results of catalysts.

| Samples                  | Surface Atomic Concentrations (%) |
|--------------------------|-----------------------------------|
|                          | Fe$^{2+}$ | Fe$^{3+}$ | Fe$_{total}$ | Ce | W | O$_{α}$ | O$_{β}$ | O$_{total}$ |
| Fe$_{85}$Ce$_{10}$W$_5$–CP–CA | 5.65      | 11.71     | 17.36       | 7.24 | 2.89 | 15.82   | 56.69   | 72.51       |
| Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$) | 5.73      | 11.83     | 17.56       | 6.33 | 2.36 | 16.09   | 57.66   | 73.75       |

Figure 6. H$_2$–temperature program reduction (H$_2$–TPR) profiles of the catalysts.

2.3.5. NH$_3$–Temperature Programmed Desorption (NH$_3$–TPD)

The peak position of NH$_3$–TPD refers to the adsorption strength, and the peaks at 100~200, 200~350 and >350 °C are attributed to the weakly acidic site, the medium-strong acid site, and the strong acid site [40], respectively. From the results in Figure 7, it can be seen that there exists weak acid sites, medium acid site, and strong acid sites on the surface of the magnetic Fe–Ce–W mixed oxide catalysts. The NH$_3$ species adsorbed on the weak acid sites and the medium acid sites were mainly assigned to the coordinated NH$_3$ bound to Lewis acid sites and the partial ionic NH$_4^+$ bound to Brønsted acid sites [41–43]. The re-introduction of nitrate decreased the adsorption of NH$_3$ on the magnetic Fe$_{85}$Ce$_{10}$W$_5$–CP–CA catalyst, particularly decreasing the intensity of its weak and medium-strong acidic sites. Combined with the results of XRD and SEM, we speculate that the re-introduction of nitrate results in a severe agglomeration of amorphous iron and tungsten species of the magnetic Fe$_{85}$Ce$_{10}$W$_5$–CP–CA catalyst, and its acid center could be covered or decompose in this process, thereby decreasing the intensity of its weak and medium-strong acidic sites. Therefore, the re-introduction of nitrate modifies the surface structure of the magnetic Fe$_{85}$Ce$_{10}$W$_5$–CP–CA catalyst, and shows better...
adsorption of the NH₃ reactants than Fe₈₅Ce₁₀W₅–CP–CA(NA₁₀) at 125~250 °C, which is considered to be a key factor in improving the low-temperature NH₃–SCR activity of the catalyst.

![Figure 7. NH₃–temperature programmed desorption (NH₃-TPD) profiles of the catalysts.](image)

2.4. Catalytic Mechanism

To identify the presence of the adsorbed NH₃ species in the SCR process on the surface of Fe₈₅Ce₁₀W₅–CP–CA, the in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra of three transient experiments were recorded under a steady-state condition, and the results are presented in Figure 8. As illustrated in Figure 8A, after NH₃ adsorption and N₂ purge at 250 °C, Fe₈₅Ce₁₀W₅–CP–CA showed several bands located at 1188, 1406, 1587, 3256, and 3351 cm⁻¹. The bands located at 1188 and 1587 cm⁻¹ can be attributed to the coordinated NH₃ on the Lewis acid sites, and the bands located at 1406 cm⁻¹ can be ascribed to the ionic NH₄⁺ bound to the Brønsted acid site, while the bands of 3256 and 3351 cm⁻¹ corresponded to the N–H stretching modes of the coordinated NH₃ connected to the Lewis acid sites [27,44–48]. After the introduction of NO + O₂ for 10 s, the adsorption peaks of the coordinated NH₃ on the Lewis acid sites (located at 1188 and 1587 cm⁻¹) and the N–H stretching modes of coordinated NH₃ connected to the Lewis acid sites (located at 3256 and 3351 cm⁻¹) disappeared, and the intensity of ionic NH₄⁺ bound to the Brønsted acid site at 1406 cm⁻¹ also became weakened. At the same time, the bidentate nitrates (1002 and 1547 cm⁻¹) disappeared. The IR bands assigned to the coordinated NH₃ also became weakened. At the same time, the bidentate nitrates (1002 and 1547 cm⁻¹) became weakened, and the band at 1560 cm⁻¹ became weakened, and the band at 1560 cm⁻¹ ascribed to the bidentate nitrates disappeared. The IR bands assigned to the coordinated NH₃ on the Lewis acid sites (1189 and 1587 cm⁻¹), the ionic NH₄⁺ bound to the Brønsted acid site (1439 cm⁻¹), and the N–H stretching modes of the coordinated NH₃ connected to the Lewis acid sites (3255 and 3364 cm⁻¹) appeared [27,47–50]. Figure 8C shows the experimental results of the introduction of NH₃ + NO + O₂ gases over Fe₈₅Ce₁₀W₅–CP–CA at 250 °C. It can clearly be seen that the IR bands ascribed to
the coordinated NH₃, the N–H stretching modes of the coordinated NH₃ and the ionic NH₄⁺ appeared, and their intensity gradually became stronger with the increase in the NH₃ + NO + O₂ introduction. However, the adsorption peaks at about 1350 and 1562 cm⁻¹ ascribed to M–NO₂ and bidentate nitrate also appeared and then quickly vanished when NH₃ + NO + O₂ gases were introduced into the reaction tank. Therefore, it can be concluded that the reaction between the adsorbed NH₃ species with gaseous NO + O₂ or the adsorbed NOₓ species might occur over Fe₈₅Ce₁₀W₅–CP–CA at 250 °C, obeyed both E–R and L–H mechanisms, and E–R was its main mechanism.

Figure 8. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of Fe₈₅Ce₁₀W₅–CP–CA catalyst under transient reactions at 250 °C. (A) Between nitrogen oxides and pre-adsorbed NH₃ species. (B) Between NH₃ and pre-adsorbed nitrogen oxides species. (C) The NH₃, NO, and O₂ species.

3. Experimental

3.1. Synthesis of the Catalyst

Fe₃(NO₃)₉·9H₂O, Ce₃(NO₃)₉·6H₂O, (NH₄)₆H₃W₁₂O₄₀·nH₂O, NH₃·H₂O, and citric acid were used as the precursors, the precipitator, and the complexing agent, respectively. For
the preparation of magnetic iron–cerium–tungsten mixed oxide catalyst through the spread self-combustion of dried gel without nitrate, a certain amount of Fe$^{III}$(NO$_3$)$_3$·9H$_2$O, Ce$^{III}$(NO$_3$)$_3$·6H$_2$O, and (NH$_4$)$_2$W$^{VI}_{12}$O$_{40}$·nH$_2$O were dissolved in the de-ionized water by keeping their molar ratio at 85:10:5. After magnetic stirring evenly, this solution was titrated into ammonia water of 2 mol/L until the pH value of 9–10. The obtained precipitation was fully washed by the de-ionized water to reduce the nitrate ion in it, and then a certain amount of citric acid was added into the washed precipitation with the molar ratio of citric acid/(Fe + Ce + W) as 1.0. After being stirred for 3 h under water bath at 50 °C, the citric acid dissolved solution were treated by microwave irradiation for 10 min with 36.4% power (microwave irradiation 8 s, 14 s suspended for a cycle with full power) using a household microwave oven (EG8MEA6-NR, 2.45 GHz, 800 W) to ignite, and this catalyst is denoted as Fe$_{85}$Ce$_{10}$W$_5$–CP–CA. The preparation of the catalyst by re-introducing nitric acid into the citric acid dissolved solution is similar to the preparation of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA, which can be expected by adding a certain amount of nitric acid into the citric acid dissolved co-precipitation precursor before the water bath, which can be denoted as Fe$_{85}$Ce$_{10}$W$_5$–CP–CA (NA$_x$, $x = 0.5, 1.0, 2.0$), where $x$ is the molar ratio of nitric acid/NO$_3^-$ in both Fe(NO$_3$)$_3$ and Ce(NO$_3$)$_3$.

3.2. Catalytic Measurement and Characterization

The catalytic measurements of NO$_x$ abatement with NH$_3$ were carried out in a one-dimensional transversely fixed quartz reactor. The simulated gas consisted of 1000 ppm NH$_3$, 1000 ppm NO, 3 vol.% O$_2$, and the balanced N$_2$ with the total flow of 2000 mL/min. The samples used in each experiment were 2 mL with a gas hourly space velocity (GHSV) of 60,000 h$^{-1}$. The concentrations of NO$_x$ and O$_2$ were monitored via a flue gas analyzer (Model 60i, Thermo Fisher Scientific Co. Ltd., Waltham, MA, USA). NO$_x$ conversion is defined by the following equation:

$$\text{NOx conversion (\%)} = \frac{C(\text{NOx})_\text{inlet} - C(\text{NOx})_\text{outlet}}{C(\text{NOx})_\text{inlet}} (1)$$

The thermal decomposition properties of the precursor before being ignited were determined with a thermal gravimetric analyzer (Netzsch, Selb, Germany, STA449 F3) under an air atmosphere. The surface morphology of the catalyst was measured on a SEM (Japan, Shimadzu). In addition, the physicochemical properties of the samples were also characterized via XRD, N$_2$ adsorption–desorption, XPS, H$_2$–TPR, and NH$_3$–TPD as the same as our previous research [27]. The average crystallite sizes of γ-Fe$_2$O$_3$ in Fe$_{85}$Ce$_{10}$W$_5$–CP–CA and Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$) were calculated according to the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos(\theta)} (2)$$

where $k$ is the shape factor ($k = 0.9$); $\lambda$ is the wavelength of radiations; and $\beta$ is the FWHM (full width at half maxima). Finally, the NH$_3$–SCR mechanism over Fe$_{85}$Ce$_{10}$W$_5$–CP–CA at 250 °C was acquired by in situ diffuse reflection infrared Fourier transform spectroscopy (in situ DRIFTS).

4. Conclusions

The nitrate brought from metal nitrates could participate in the spread self-combustion of citric acid dried gel. The removal of nitrate contributes to optimize the structure properties and acid sites of the magnetic Fe–Ce–W mixed oxide catalyst. The removal of nitrate helps in the formation of dispersive gamma-Fe$_2$O$_3$ in Fe$_{85}$Ce$_{10}$W$_5$–CP–CA, accelerating the crystallite rate and refining the particle size, and it shows a wider pore size distribution than Fe$_{85}$Ce$_{10}$W$_5$–CP–CA(NA$_{1.0}$). At the same time, the removal of nitrate also enhances the concentrations of cerium/tungsten on the surface of the magnetic catalyst and its low-temperature adsorption of NH$_3$. Therefore, the re-introduction of nitrate decreases the low-temperature NH$_3$–SCR activity of Fe$_{85}$Ce$_{10}$W$_5$–CP–CA, and both E–R and L–H mechanisms exist over Fe$_{85}$Ce$_{10}$W$_5$–CP–CA at 250 °C.
Author Contributions: Formal analysis, S.-m.W.; Investigation, B.Y.; Resources, W.L.; Writing-original draft, X.N.; Writing-review & editing, Z.-b.X. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Bin Yang grant number No. 2016YFB0600601, Zhi-bo Xiong grant number No. 51406118 and Wei Lu grant number No. QD2015017. And The APC was funded by Bin Yang.

Acknowledgments: This work was supported by the National Key Research and Development Program of China (No. 2016YFB0600601), the National Science Foundation of China (No. 51406118), and the Program of Special Appointment (Eastern Scholar) at the Shanghai Institutions of Higher Learning (No. QD2015017).

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

References
1. Parvulescu, V.; Delmon, B.; Grange, P. Catalytic removal of NO. Catal. Today 1998, 46, 233–316. [CrossRef]
2. Forzatti, P.; Nova, I.; Tronconi, E. Enhanced NH3 selective catalytic reduction for NOx abatement. Angew. Chem. Int. Edit. 2009, 48, 8366–8368. [CrossRef] [PubMed]
3. Husain, D. Chemistry of atmospheres: An introduction to the chemistry of atmospheres of earth the planets and their satellites by R. P. Wayne. J. Photo. Chem. Photobiol. A Chem. 1992, 63, 253–254. [CrossRef]
4. Zhao, S.J.; Wang, L.; Wang, Y.; Li, X. Hierarchically porous LaFeO3 perovskite prepared from the pomelo peel bio-template for catalytic oxidation of NO. J. Phys. Chem. Solids 2018, 116, 43–49. [CrossRef]
5. Amanatidis, S.; Ntziachristos, L.; Giechaskiel, B.; Bergmann, A.; Samaras, Z. Impact of selective catalytic reduction on exhaust particle formation over excess ammonia events. Environ. Sci. Technol. 2014, 48, 11527–11534. [CrossRef]
6. Gu, Q.; Wang, L.; Wang, Y.; Li, X. Effect of praseodymium substitution on La1-xPrxMnO3 (x=0-0.4) perovskites and catalytic activity for NO oxidation. J. Phys. Chem. Solids 2019, 133, 52–58. [CrossRef]
7. Ning, P.; Song, Z.X.; Li, H.; Zhang, Q.L.; Liu, X.; Zhang, J.H.; Tang, X.S.; Huang, Z.Z. Selective catalytic reduction of NO with NH3 over CeO2-ZrO2-WO3 catalysts prepared by different methods. Appl. Surf. Sci. 2015, 332, 130–137. [CrossRef]
8. Shang, D.H.; Zhong, Q.; Cai, W. High performance of NO oxidation over Ce-Co-Ti catalyst: The interaction between Ce and Co. Appl. Surf. Sci. 2013, 325, 211–216. [CrossRef]
9. Dunn, J.P.; Koppula, P.R.; Stenger, H.G.; Wachs, I.E. Oxidation of sulfur dioxide to sulfur trioxide over supported vanadia catalysts. Appl. Catal. B 1998, 19, 103–117. [CrossRef]
10. Balingari, T.; Ettireddy, P.R.; Somogyvari, A.; Liu, Y.; Vorontsov, A.; McDonald, C.A.; Smirniotis, P.G. Influence of elevated surface texture hydrated titania on Ce-doped Mn/TiO2 catalysts for the low-temperature SCR of NOx under oxygen-rich conditions. J. Catal. 2015, 325, 145–155. [CrossRef]
11. Narasimharao, K.; Malik, M.A.; Mokhtar, M.M.; Basahel, S.N.; Al-Thabaiti, S.A. Iron oxide supported sulfated TiO2 nanotube catalysts for NO reduction with propane. Ceram. Int. 2014, 40, 4039–4053. [CrossRef]
12. Jiang, Y.; Gao, X.; Zhang, Y.X.; Wu, W.H.; Song, H.; Luo, Z.Y.; Cen, K.F. Effects of PbCl2 on selective catalytic reduction of NO with NH3 over vanadia-based catalysts. J. Hazard. Mater. 2014, 274, 270–287. [CrossRef] [PubMed]
13. Kröcher, O.; Elesner, M. Chemical deactivation of V2O5-WO3/TiO2 SCR catalysts by additives and impurities from fuels, lubrication oils, and urea solution: I. catalytic studies. Appl. Catal. B 2008, 77, 215–227. [CrossRef]
14. Li, X.D.; Wang, C.; Huang, J.Q.; Yuan, Y.; Wang, B.; Zhang, H.B.; Xia, F.; Xiao, J.Z. The effects of Cu-content on Mg2Cu3Fe1O15-x electrodes for YSZ-based mixed-potential type NH3 sensors. Ceram. Int. 2016, 42, 9363–9370. [CrossRef]
15. Balle, P.; Geiger, B.; Kureti, S. Selective catalytic reduction of NOx by NH3 on Fe/HBEA zeolite catalysts in oxygen-rich exhaust. Appl. Catal. B 2009, 85, 109–119. [CrossRef]
16. Duan, L.B.; Duan, Y.; Sarbassov, Y.; Li, Y.; Anthony, E. SO3 formation under oxy-CFB combustion conditions. Int. J. Greenh. Gas Con. 2015, 43, 172–178. [CrossRef]
17. Zhao, S.J.; Wang, Y.; Wang, L.; Jin, Y.L. Preparation, characterization and catalytic application of hierarchically porous LaFeO3 from a pomelo peel template Inorg. Chem. Front. 2017, 4, 994–1002.
18. Chen, J.; Duan, L.; Donat, F.; Müller, C.; Anthony, E.; Fan, M. Self-activated nanostructured composite for improved CaL-CLC technology. Chem. Eng. J. 2018, 351, 1038–1046. [CrossRef]
19. Kazantsev, P.A.R.V.; Pankina, G.V.; Maslakov, K.I.; Lunin, B.S.; Eliseev, O.L. Carbon-Silica composite as an effective support for iron fischer-tropsch synthesis catalysts. Energy Technol. 2019, 7, 1800961.
20. Chen, J.; Duan, L.; Sun, Z. Accurate control of cage-Like CaO hollow microspheres for enhanced CO₂ capture in calcium looping via a template-assisted synthesis approach. Environ. Sci. Technol. 2019, 53, 2249–2259. [CrossRef]

21. Wu, D.; Shi, Z.F.; Zhang, X.P.; Wu, X.H. Progress of studies on preparation of TiO₂ photocatalysts with sol-gel auto igniting synthesis. Earth Environ. Sci. 2017, 94, 1–4. [CrossRef]

22. Parida, K.M.; Reddy, K.H.; Martha, S.; Das, N.; Bisawal, N. Fabrication of nanocrystalline LaFeOₓ: An efficient sol–gel auto-combustion assisted visible light responsive photocatalyst for water decomposition. Int. J. Hydrogen Energy 2010, 35, 12161–12168. [CrossRef]

23. Siyo, A.K. Magnetic and structural properties of CoCrₓFe₂₋ₓO₄ spinels prepared by solution self-combustion method. Ceram. Int. 2017, 43, 2288–2290. [CrossRef]

24. Cannas, C.; Musinu, A.; Peddis, D.; Piccaluga, G. New synthesis of ferrite-silica nanocomposites by a sol-gel auto-combustion. J. Nanopart. Res. 2004, 6, 223–232. [CrossRef]

25. Kaitlyn, A.; George, K.S. Synthesis of GAGG: Ce³⁺ powders for ceramics using mechanochemical and solution combustion methods. J. Am. Ceram. Soc. 2018, 101, 3837–3849.

26. Yeh, C.L.; Ke, C.Y. Synthesis of TiB₂-Al₂O₃-FeAl composites via self-sustaining combustion with Fe₂O₃/TiO₂-based thermite mixtures. Ceram. Int. 2018, 44, 16030–16034. [CrossRef]

27. Xiong, Z.B.; Ning, X.; Zhou, F.; Yang, B.; Tu, Y.W.; Jin, J.; Lu, W.; Liu, Z.H. Environment-friendly magnetic Fe-Ce-W catalyst for the selective catalytic reduction of NO with NH₃: Influence of citric acid content on its activity-structure relationship. RSC Adv. 2018, 8, 21915–21925. [CrossRef]

28. Ianoș, R.; Tăcuulescu, A.; Păcurar, C.; Lazău, I. Solution combustion synthesis and characterization of magnetite, Fe₃O₄, nanoparticles. J. Am. Ceram. Soc. 2012, 95, 2236–2240. [CrossRef]

29. Ianoș, R.; Moacă, E.A.; Căpăraru, A.; Lazău, R.; Păcurar, C. Maghemite, γ-Fe₂O₃, nanoparticles preparation via carbon-templated solution combustion synthesis. Ceram. Int. 2018, 44, 14090–14094. [CrossRef]

30. Zhao, J.; Liang, Y.; Yan, H.; Gu, A.; He, S.; Liu, J. Preparation of nano-MnZn ferrite by gel-self-combustion technique. J. Mater. Sci. Eng. 2003, 21, 68–71.

31. Xu, L.T.; Niu, S.L.; Lu, C.M.; Zhang, Q. Influence of calcination temperature on Fe₃O₄-MgO₂O₂ catalyst for selective catalytic reduction of NO with NH₃. Fuel 2018, 219, 248–258. [CrossRef]

32. Zhao, K.; Meng, J.P.; Lu, J.Y.; He, Y.; Huang, H.Z.; Tang, Z.C.; Zhen, X.P. Sol-gel one-pot synthesis of efficient and environmentally friendly iron-based catalysts for NH₃-SCR. Appl. Surf. Sci. 2018, 445, 454–461. [CrossRef]

33. Zhang, Q.L.; Liu, X.; Ning, P.; Song, Z.X. Enhanced performance in NO₂ reduction by NH₃ over a mesoporous Ce-Ti-MoOₓ catalyst stabilized by a carbon template. Catal. Sci. Technol. 2015, 5, 2260–2269. [CrossRef]

34. Liu, F.D.; He, H. Structure-activity relationship of iron titanate catalysts in the selective catalytic reduction of NOₓ with NH₃. J. Phys. Chem. C 2010, 114, 16929–16936. [CrossRef]

35. Wang, R.N.; Wu, X.; Zou, C.L.; Li, X.J.; Du, Y.L. NO₂ removal by selective catalytic reduction with ammonia over a hydrotalcite-derived NiFe mixed oxide. Catalysts 2018, 8, 384. [CrossRef]

36. Tan, J.B.; Wei, Y.C.; Sun, Y.Q.; Liu, J.; Zhao, Z.; Song, W.Y.; Li, J.M.; Zhang, X. Simultaneous removal of NOₓ and soot particulates from diesel engine exhaust by 3DOM Fe-Mn oxide catalysts. J. Ind. Eng. Chem. 2018, 63, 84–94. [CrossRef]

37. Wang, H.; Ning, P.; Zhang, Q.; Liu, X.; Zhang, T.; Fan, J.; Wang, J.; Long, K. Promotional mechanism of WO₃ over RuO₂-Fe₂O₃ catalyst for NH₃-SCO reaction. Appl. Catal. A 2018, 561, 158–167. [CrossRef]

38. Wang, H.; Qu, Z.P.; Xie, H.B.; Maeda, N.; Lei, M.; Wang, Z. Insight into the mesoporous FeₓCe₁₋ₓO₂₋₅ catalysts for selective catalytic reduction of NO with NH₃: Regulable structure and activity. J. Catal. 2016, 338, 56–67. [CrossRef]

39. Abolfazl, B.R.; Rezaee, M. Low temperature CO oxidation over Fe-Co mixed oxide nanocatalysts. Chem. Eng. J. 2012, 184, 141–146.

40. Li, X.S.; Li, K.; Yue, Z.P.; Li, X.Y.N.; Zhang, D.; Wang, J.J.; Chen, J.; Li, H. Interaction of phosphorus with a FeTiO₃ catalyst for selective catalytic reduction of NOₓ with NH₃: Influence on surface acidity and SCR mechanism. Chem. Eng. J. 2018, 347, 173–183. [CrossRef]

41. Xiong, Z.B.; Liu, J.; Zhou, F.; Liu, D.Y.; Lu, W.; Jin, J.; Ding, S.F. Selective catalytic reduction of NOₓ over iron-cerium-tungsten mixed oxide catalyst prepared by different methods. Appl. Surf. Sci. 2017, 406, 218–225. [CrossRef]
42. Xiong, Z.B.; Bai, P.; Zhou, F.; Wu, C.; Lu, W.; Jin, J.; Ding, S.F. Magnetic iron-cerium-tungsten mixed oxide pellets prepared through critic acid sol-gel process assisted by microwave irradiation for selective catalytic reduction of NOx with NH3. *Powder Technol.* 2017, 319, 19–25. [CrossRef]

43. Li, X.; Li, J.H.; Yue, P.; Xu, B. Selective catalytic reduction of NO with NH3 over novel iron-tungsten mixed oxide catalyst in a broad temperature range. *Catal. Sci. Technol.* 2015, 5, 4556–4564. [CrossRef]

44. Zhang, G.; Ren, J.J.; Liu, B.L.; Tian, M.; Zhou, H.W.; Zhao, J.S. In situ hydrothermal preparation and photocatalytic desulfurization performance of metallophthalocyanine sensitized SnO2. *J. Inorg. Chim. Acta* 2018, 471, 782–787. [CrossRef]

45. Liu, Y.; Gu, T.T.; Weng, X.L.; Wang, Y. DRIFT studies on the selectivity promotion mechanism of Ca-modified Ce-Mn/TiO2 catalysts for low-temperature NO reduction with NH3. *J. Phys. Chem. A* 2012, 116, 16582–16592. [CrossRef]

46. Chen, P.; Tao, L.; Zhu, J.; Zhao, G.; Liu, Y.; Lu, Y. Morphology-controllable hexagonal-phase indium oxide in situ structured onto a thin-felt Al2O3/Al-fiber for the hydrogenation of CO2 to methanol. *Energy Technol.* 2019, 7, 1800747. [CrossRef]

47. Liu, J.; Xiong, Z.B.; Zhou, F.; Lu, W.; Jin, J.; Ding, S.F. Promotional effect of H2O2 modification on the cerium-tungsten-titanium mixed oxide catalyst for selective catalytic reduction of NO with NH3. *J. Phys. Chem. Solids* 2018, 121, 360–366. [CrossRef]

48. Castellanos, I.; Marie, O. An operando FT-IR study of the NOx SCR over Co-HFER and Fe-HFER using acetylene as a reducing agent. *Catal. Today* 2017, 283, 54–65. [CrossRef]

49. Shi, J.; Zhang, Y.; Zhang, Z.H.; Fan, Z.Y.; Chen, M.X.; Zhang, Z.X.; Shangguan, W.F. Water promotion mechanism on the NH3-SCR over Fe-BEA catalyst. *Catal. Commun.* 2018, 115, 59–63. [CrossRef]

50. Devadas, M.; KroCher, O.; Elsener, M.; Wokaun, A.; Mitrikas, G.; Söger, N.; Pfeifer, M.; Demel, Y.; Mussmann, L. Characterization and catalytic investigation of Fe-ZSM5 for urea-SCR. *Catal. Today* 2007, 119, 137–144. [CrossRef]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).