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A Study on Mn-Fe Catalysts Supported on Coal Fly Ash for Low-Temperature Selective Catalytic Reduction of NO_x in Flue Gas

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Abstract: A series of Mn_{0.15}Fe_{0.05}/fly-ash catalysts have been synthesized by the co-precipitation method using coal fly ash (FA) as the catalyst carrier. The catalyst showed high catalytic activity for low-temperature selective catalytic reduction (LTSCR) of NO with NH₃. The catalytic reaction experiments were carried out using a lab-scale fixed-bed reactor. De-NO_x experimental results showed the use of optimum weight ratio of Mn/FA and Fe/FA, resulted in high NH₃-SCR (selective catalytic reduction) activity with a broad operating temperature range (130–300 °C) under 50000 h^{−1}. Various characterization methods were used to understand the role of the physicochemical structure of the synthesized catalysts on their De-NO_x capability. The scanning electron microscopy, physical adsorption-desorption, and X-ray photoelectron spectroscopy showed the interaction among the MnO_x, FeO_x, and the substrate increased the surface area, the amount of high valence metal state (Mn⁴⁺, Mn³⁺, and Fe³⁺), and the surface adsorbed oxygen. Hence, redox cycles (Fe³⁺ + Mn²⁺ ↔ Mn³⁺ + Fe²⁺; Fe²⁺ + Mn⁴⁺ ↔ Mn³⁺ + Fe³⁺) were co-promoted over the catalyst. The balance between the adsorption ability of the reactants and the redox ability can promote the excellent NO_x conversion ability of the catalyst at low temperatures. Furthermore, NH₃/NO temperature-programmed desorption, NH₃/NO-thermo gravimetric-mass spectrometry (NH₃/NO-TG-MS), and in-situ DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) results showed the Mn_{0.15}Fe_{0.05}/FA has relatively high adsorption capacity and activation capability of reactants (NO, O₂, and NH₃) at low temperatures. These results also showed that the Langmuir–Hinshelwood (L–H) reaction mechanism is the main reaction mechanism through which NH₃-SCR reactions took place. This work is important for synthesizing an efficient and environmentally-friendly catalyst and demonstrates a promising waste-utilization strategy.

Keywords: coal fly ash; Mn_{0.15}Fe_{0.05}/FA catalysts; low-temperature SCR; De-NO_x efficiency; co-impregnation method

1. Introduction

Coal, as a fuel, has played a vital role in the development of the world's economy. Coal fly ash production resulting from coal combustion is ecologically problematic, and every year millions of tons of fly ash are produced [1]. Also, the emission of environmentally harmful gases, e.g., NO_x, has been a global concern, where coal combustion is responsible for most of the emissions. In 2017, the NO_x emissions of China alone reached 12.59 million tons, with 67.6% from stationary sources (China Statistical Yearbook 2019). High concentrations of NO_x gases in the atmosphere is environmentally

problematic, which is directly responsible for photochemical smog, ozone deterioration, and acid rain [2,3]. With the implementation of strict environmental policies, the NO_x emissions of coal-fired power plants have been limited to $100 \text{ mg}\cdot\text{m}^{-3}$ (GB13223-2011). Other factories like steel refineries (GB28662-2012) and cement plants (GB4915-2013) are limited to $300 \text{ mg}\cdot\text{m}^{-3}$, while glass factories get $700 \text{ mg}\cdot\text{m}^{-3}$ (GB26453-2011).

Currently, selective catalytic reduction by NH_3 (NH_3 -SCR) is a developed and effective technology studied for many years. Typically, NH_3 -SCR catalysts contain a mixture of metal ions, and V-W (Mo)/Ti catalyst is the most efficient commercial SCR catalyst [4]. The catalyst unit is usually placed upstream of the electrostatic precipitator (ESP) and desulfurization unit because of its high operating temperature ($300\text{--}400^\circ\text{C}$). This placement shortens the catalyst's life due to poisoning by fly ash and sulfur dioxide present in the flue gas. This issue has been addressed by placing the catalyst downstream the ESP and desulfurization unit. While the temperatures in the downstream unit are significantly below the activation temperature of the commercial catalyst (V-W (Mo)/Ti), the way to mitigate this issue is either by pre-heating the flue gas or by changing the tail system, which is a significant financial burden [5]. Therefore, there is the necessity for an efficient and environmentally-friendly catalyst, which has a low-temperature activation ($<200^\circ\text{C}$) that can effectively be placed downstream of the ESP and desulfurization unit.

Until recent years, transition metals have gained considerable attention for their excellent catalytic property. Mn-based catalysts have attracted significant attention due to their great low-temperature De- NO_x capability and the diversity of valence states [2,6]. However, the introduction of another transition metal could further increase the NH_3 -SCR ability at low temperatures, such as the combination of manganese and iron. Many studies have used the hydrothermal impregnation method to synthesize catalysts with special morphological structure, such as Fe-OMS-2 with a uniform nanowire morphology [7], MnFe-MOF-74 [8], MnO_x - FeO_x nanoneedles [9], MnFe nanowire [10], MnFeO_x nanorod [11], MnCeFeTiO_x microsphere, and MnFeO_x -MOFs [12]. Some other studies have coprecipitated Mn-Fe into different commercial carriers [2,6,8,13,14], such as FeMnTiO_x [6], Mn-Fe/ TiO_2 [13], Fe-Mn/SBA-15 [14], and Mn-Fe@ceramics [8]. These catalysts can achieve a maximum NO_x conversion of 86.8% at 210°C . Furthermore, López-Hernández et al. [15] prepared a series of Mn-Fe catalysts loaded on different carriers and found that the activity of the catalysts is highly dependent on the structure and acidity of the carriers. Therefore, the carrier selected is of high importance, influencing the performance of the catalyst. However, there are still some setbacks for SCR technology: They are expensive, time-consuming, and complex.

In recent years, the accumulation of large quantities of FA has caused significant ecological challenges; every year, 800 million tons of FA is produced worldwide [1]. In China, about 67% of FA is used in various industries. The remaining FA is mostly disposed of under the dams during construction, threatening living organisms [16]. Thus, a safe and cost-effective technique is vital to utilize excess FA. Value-added products are among the best strategies researchers have been employing to convert FA into high-value materials [17], such as arsenic adsorbent [18] and wastewater treatment agents [19]. Chen et al. [20] synthesized a catalyst by loading Mn-Ce oxides on pretreated-FA, which had an operating temperature range of $200\text{--}300^\circ\text{C}$. Li et al. [14] used FA to produce a molecular sieve (SBA-15) and then used the impregnation method to synthesis Fe-Mn/SBA-15 catalyst, which possessed an excellent De- NO_x activity in the temperature range of $180\text{--}300^\circ\text{C}$ [21]. In another study, the authors used the co-precipitation method to load Mn-Ce onto a carrier composed of a mixture of FA and Ca-based bentonite to synthesize a catalyst that could adsorb and reduce NO at 60% for 18 min. Cui et al. [22] used sulfuric acid to activate fly ash as a silica-based sulfuric acid catalyst, which could achieve SO_2 and NO removal by H_2O_2 gas. Although significant research efforts have been focused on the utilization of FA as De- NO_x catalyst, the literature still lacks an intuitive, cost-effective, and environmentally-friendly catalyst with excellent catalytic performance.

From the economic point of view, and based on the previous studies, we present an intuitive one-step co-impregnation method to prepare a group of $\text{Mn}_x\text{Fe}_y/\text{FA}$ catalysts with excellent NH_3 -LTSCR

efficiency. This catalyst could solve two of the most important setbacks of coal combustion, where the produced waste FA, after simple treatment, could be used to remove NO_x from flue gas emissions through a straightforward, environmentally-friendly and cost-effective synthesis method. Also, the catalytic performance and reaction pathways were determined by various characterization methods.

2. Results and Discussion

2.1. The Morphology and Structure of Catalysts

The physical structure of the catalysts was studied by SEM technique and the N_2 physisorption analysis. The results are given in Figures S1 and S2 (summarized in Table 1). These results correlate to a great extent. From the SEM images (Figure S1) of the various catalysts, a large number of debris or/and cracks can be observed on the surface. FA had a smooth surface with minimum irregularities resulting in low surface area ($7.7 \text{ m}^2\cdot\text{g}^{-1}$) and total pore volume ($0.1 \text{ cm}^3\cdot\text{g}^{-1}$). $\text{Fe}_{0.10}/\text{FA}$ had larger openings or holes on the surface. Its surface area and total pore volume reached $35.8 \text{ m}^2\cdot\text{g}^{-1}$ and $0.1 \text{ cm}^3\cdot\text{g}^{-1}$, respectively. The presence of micro-particles on $\text{Mn}_{0.15}/\text{FA}$ surface resulted in a high surface area value of $78.0 \text{ m}^2\cdot\text{g}^{-1}$. For $\text{Mn}_x\text{Fe}_{0.10}/\text{FA}$, when the loading amount of Mn was lower than 0.15, more pores were observed. However, when Mn content was further increased to 0.20, dense and bonding pores were formed. For $\text{Mn}_{0.15}\text{Fe}_y/\text{FA}$, when the loading amount of Fe/FA was lower than 0.1, less porous structures were formed. The increase of FeO_x led to the formation of a highly porous structure. In comparison, the surface morphology of $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ varied significantly with the growth of numerous screw-like structures appearing on the surface, as shown in Figure S1g, resulting in a high surface area value of $91.6 \text{ m}^2\cdot\text{g}^{-1}$ and a total pore volume of $0.15 \text{ cm}^3\cdot\text{g}^{-1}$. The interaction between MnO_x , FeO_x , and the carrier changes the micro-morphology and the physical structure of the samples [23,24].

Table 1. Surface species and physical properties of $\text{Mn}_x\text{Fe}_y/\text{FA}$ samples.

Sample	Elements/wt.% ^a		Surface Atomic Concentration/% ^b			Physical Properties ^c			The Average Crystallite Size of SiO_2 (nm) ^d
	Fe/FA	Mn/FA	Fe	Mn	O	S_{BET} (m^2/g)	Average Pore Size (nm)	V_{Total} (cm^3/g)	
FA	4.5	0.1	2.2	6.6	91.2	7.7	12.7	0.1	71.1
$\text{Mn}_{0.15}/\text{FA}$	3.1	15.1	1.5	15.2	83.3	78.0	3.1	0.1	62.7
$\text{Fe}_{0.10}/\text{FA}$	13.4	0.1	12.2	1.8	88.7	35.8	6.5	0.1	49.8
$\text{Mn}_{0.05}\text{Fe}_{0.10}/\text{FA}$	13.7	5.0	9.6	6.9	83.5	46.4	5.4	0.1	52.4
$\text{Mn}_{0.15}\text{Fe}_{0.10}/\text{FA}$	10.8	14.4	5.9	16.7	77.4	85.3	3.5	0.2	57.7
$\text{Mn}_{0.20}\text{Fe}_{0.10}/\text{FA}$	13.0	19.7	5.5	22.4	72.2	64.6	4.6	0.2	70.5
$\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$	8.5	14.9	3.8	16.1	80.1	91.6	3.4	0.2	53.1

^a Element compositions measured by using ICP-OES; ^b Surface atomic concentration calculated by XPS; ^c Physical properties calculated by N_2 physisorption. ^d Crystallite size of SiO_2 calculated by the Debye-Scherrer equation.

The N_2 physisorption analysis was used to understand the change of the physical structure of the catalysts caused by metal oxides. The N_2 adsorption/desorption isotherms of different samples are given in Figure S2. Notably, the curves of all samples are following the type IV isotherms with type H3 hysteresis loops, which corresponds to the micro- and mesoporous structure [25,26]. The presence of micro- and mesoporous structure is evident in Figure S2, indicating that the majority of the pores have an opening pore diameter of 6 nm. The main factor contributing to the formation of these micro- and mesoporous structures is the diffusion of iron oxides and manganese oxide into the lattice of the carrier during the calcination process [23]. These mesoporous materials provide abundant active sites for the adsorption of reactants, which facilitates the mass transfer process at the gas-solid phase boundary [26]. Efficient mass transfer plays a vital role during the bulk reaction and lowering the energy required for the NH_3 -SCR reaction. The N_2 desorption capacity of all samples followed the order of $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA} > \text{Mn}_{0.15}/\text{FA} > \text{Fe}_{0.10}/\text{FA} > \text{FA}$. It is evident that, with the doping of metal

oxide, the internal structure of samples became more copious than that of the FA, and the larger specific surface area of $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ provides more active sites than others.

2.2. Catalytic Reactivity during Low-Temperature SCR Reactions

Figure 1 shows the catalytic activities of $\text{Mn}_x\text{Fe}_y/\text{FA}$ catalysts at different temperatures. Where x is the weight ratio of Mn to FA, and y is the weight ratio of Fe to FA. The activity of $\text{Fe}_{0.10}/\text{FA}$ by Mn doping with “ x ” ranging from 0.05 to 0.2 at a GHSV of $50,000 \text{ h}^{-1}$ is shown in Figure 1a. The as-obtained FA showed a weak De- NO_x activity at the designed experimental temperatures, with the highest De- NO_x efficiency of $\sim 23.95\%$ recorded at 300°C . This is due to the natural structure and surface property of FA [15], which will be demonstrated in the following sections. After the addition of Fe (weight ratio of 0.10), slightly higher De- NO_x activity was recorded. These results indicate that the introduction of Fe did not contribute much to the De- NO_x activity of $\text{Fe}_{0.10}/\text{FA}$. However, the introduction of Mn into $\text{Fe}_{0.10}/\text{FA}$ notably improved its SCR activity, and the graphed NO_x conversion data of all the samples show a “volcanic” shape (Figure 1a). As the ratio of Mn was increased to 0.15, De- NO_x activity increased, and further addition of Mn led to a decrease in conversion efficiency. De- NO_x efficiency of different samples increased as follows: $\text{FA} < \text{Fe}_{0.10}/\text{FA} < \text{Mn}_{0.05}\text{Fe}_{0.10}/\text{FA} < \text{Mn}_{0.20}\text{Fe}_{0.10}/\text{FA} < \text{Mn}_{0.10}\text{Fe}_{0.10}/\text{FA} < \text{Mn}_{0.15}\text{Fe}_{0.10}/\text{FA}$. The temperature range in which the NO_x conversion efficiency reaches 80% (T_{80}) was considered as a primary indicator, and when conversion efficiency has reached 50% (T_{50}), that temperature is considered as the activation temperature of NH_3 -SCR activity. Among these samples, the catalytic activity of $\text{Mn}_{0.15}\text{Fe}_{0.10}/\text{FA}$ shows high conversion efficiency, with the lowest T_{50} at 108°C and the broadest T_{80} at $145\text{--}300^\circ\text{C}$. Indicating that $\text{Mn}_{0.15}\text{Fe}_{0.10}/\text{FA}$ exhibits great potential as an LTSCR catalyst ($100\text{--}250^\circ\text{C}$), and the mass ratio of Mn/FA was fixed at 0.15.

Figure 1. NO_x Conversion during the NH_3 -SCR process over $\text{Mn}_x\text{Fe}_{0.10}/\text{FA}$ with different Mn content ($x = 0, 0.05, 0.10, 0.15$, and 0.20) (a) and $\text{Mn}_{0.15}\text{Fe}_y/\text{FA}$ with different Fe content ($y = 0, 0.04, 0.05, 0.06$, and 0.10) (b); and the stability of the $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ catalyst at 200°C (c). Experimental conditions: 1000ppm of NO , 1000ppm of NH_3 , 5 vol.% O_2 and N_2 as the balance gas, GHSV of $50,000 \text{ h}^{-1}$.

Then, the ratio of FeO_x in the $\text{Mn}_{0.15}\text{Fe}_y/\text{FA}$ catalyst was varied and optimized to improve its efficiency and obtain the most efficient LTSCR catalyst. The De- NO_x activity of $\text{Mn}_{0.15}\text{Fe}_y/\text{FA}$ is given in Figure 1b. Compared with $\text{Mn}_{0.15}/\text{FA}$, the NO_x efficiency of all catalysts was further improved at the desired temperatures (100–300 °C). The conversion efficiency improved as the Fe content increased to 0.05, and then declined with a further increase in the ratio of Fe. The best activity was obtained from the $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ during the whole operating temperature range, which has the lowest T_{50} (100 °C) and the broadest T_{80} (130–300 °C). Moreover, over 90% of NO_x conversion was obtained between 147 and 300 °C. The final weight ratio of FeO_x (0.05) and MnO_x (0.15) achieved a high catalytic activity. In comparison (Table 2), the $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ has been successfully synthesized by a straightforward method. The stability results of the catalyst are shown in Figure 1c. It can be seen that after 4 hours and three cycles, the $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ catalyst exhibited excellent stability with long stable catalytic activity and good regenerability.

Table 2. Summary of typical MnFeO_x oxide catalysts used for the NH_3 -SCR process.

Catalyst	Prepared	NO_x Conversion (T_{80})	Reaction Condition	Ref.
$\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$	Co-precipitation	130–300 °C	$[\text{NO}] = [\text{NH}_3] = 1000 \text{ ppm}$, $[\text{O}_2] = 5 \text{ vol.}\%$, GHSV = 50,000 h^{-1}	This work
11.2Fe-11Mn/SBA-15	Wetness impregnation	180–325 °C	$[\text{NO}] = [\text{NH}_3] = 300 \text{ ppm}$, $[\text{O}_2] = 3 \text{ vol.}\%$, GHSV = ~120,000 h^{-1}	[14]
Mn-Fe/ Al_2O_3	Incipient wetness impregnation	300 °C	$[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 4 \text{ vol.}\%$, GHSV = ~90,000 $\text{mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[15]
$\text{MnCeFeO}_x\text{-AC}$	Impregnation	100–225 °C	$[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 11 \text{ vol.}\%$, GHSV = 12,000 h^{-1}	[9]
Tourmaline-modified FeMnTiO_x	Sol-gel	175–375 °C	$[\text{NO}] = [\text{NH}_3] = 800 \text{ ppm}$, $[\text{O}_2] = 8 \text{ vol.}\%$, GHSV = 50,000 h^{-1}	[27]
FeMnO_x Mn-rich limonite	Thermal activation	130–300 °C	$[\text{NO}] = [\text{NH}_3] = 1000 \text{ ppm}$, $[\text{O}_2] = 3 \text{ vol.}\%$, GHSV = 72,000 h^{-1}	[28]
MnCeFeTiO_x micro-spherical	Co-precipitation and spray drying	170–320 °C	$[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 5 \text{ vol.}\%$, GHSV = 40,000 h^{-1}	[29]
MnFeO_x nanorod	Hydrothermal	130–400 °C	$[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 5 \text{ vol.}\%$, GHSV = 28,000 h^{-1}	[11]
MnFe nanowire	Electrospinning	180–330 °C	$[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 5 \text{ vol.}\%$, GHSV = 36,000 h^{-1}	[10]
$\text{MnFeO}_x\text{-MOFs}$	Hydrothermal reaction-calcination	150–270 °C	$[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 5 \text{ vol.}\%$, GHSV = 10,000 h^{-1}	[8]

2.3. Reaction Mechanism Analysis

2.3.1. Surface Chemical States

The XRD (X-ray Diffraction) results of the $\text{Mn}_x\text{Fe}_y/\text{FA}$ catalysts are shown in Figure S3. For FA, only the diffraction peaks of SiO_2 and weaker Fe_2O_3 were observed. As different ratios of Mn and Fe oxide were doped, no additional peaks besides those of FA were detected. However, ICP-OES (Inductively Coupled Plasma Optical Emission spectroscopy) results (Table 1) show that the mass content of Fe and Mn within all samples is approximately equal to the calculated values, which indicates that the added metal oxide is present in the catalyst. XRD results also showed that the intensity of peaks and the average crystal size assigned to SiO_2 decreased with Mn and Fe doping, and the peak of SiO_2 slightly shifted towards lower 2θ values. The average crystal size of SiO_2 was calculated based on the diffraction peak (1,0,0) according to the Scherrer formula (Table 1). These results indicated that the presence of defective lattice and a decrease in the crystalline size of SiO_2 , which were caused by the introduction of Mn and Fe oxide. This result also shows the strong interaction between $\text{FeO}_x/\text{MnO}_x$ and the carrier. The defective lattice and the interaction between metal oxides and the carrier led to a more unbalance charge state and oxygen vacancy, providing abundant active sites during the SCR process and contributing to the higher NO conversion ability of the catalyst [5].

The valence state of the added metals is of significant importance in the SCR reaction. To further examine the surface chemical states and the types of ion species over catalysts, XPS (X-ray photoelectron spectroscopy) measurement of Fe 2p, Mn 2p, and O 1s in fresh catalysts were conducted (Table 1). The results indicate that the surface concentration of Mn is slightly higher than that in bulk catalysts (from the ICP-OES results), while the concentration of Fe shows the opposite phenomenon. This indicates that Fe could promote the enrichment of Mn on the surface, providing more active sites during low-temperature De-NO_x by NH₃. The recorded spectra of different elements were fitted into multiple sub-bands according to the multivalent oxide species on the surface by Gaussian-Lorentz fitting of XPS Peak 4.1, and examples of a peak-fitted graph are given in Figure S4. The relative atomic ratios of different elemental states are listed in Table 3.

Table 3. The surface elemental concentration of catalysts by XPS analysis.

Catalyst	Mn 2 p _{3/2} (eV)		Fe 2 p _{3/2} (eV)	O 1s (eV)		
	Mn ⁴⁺ /Mn ⁿ⁺	Mn ³⁺ /Mn ⁿ⁺	Fe ³⁺ /Fe ⁿ⁺	O _{surf} /O _t	O _{ads} /O _t	O _α /O _t
Fe _{0.10} /FA	-	-	66.21	23.94	48.85	72.79
Mn _{0.05} Fe _{0.10} /FA	33.44	48.98	69.99	23.65	47.59	71.24
Mn _{0.15} Fe _{0.10} /FA	36.92	49.18	69.38	16.27	46.88	63.15
Mn _{0.20} Fe _{0.10} /FA	33.26	49.21	52.27	17.31	44.36	61.67
Mn _{0.15} /FA	37.09	48.13	-	29.26	44.17	73.43
Mn _{0.15} Fe _{0.05} /FA	39.59	48.38	65.45	22.78	42.4	65.18

The overlapped Mn 2p peaks were deconvoluted into three pairs of peaks. The fitted peaks are assigned to Mn⁴⁺ (643.58 and 654.71 eV), Mn³⁺ (642.26 and 653.6 eV), and Mn²⁺ (641.21 and 652.5 eV). Figure S4a shows that three valence states of Mn species within the series of Mn_xFe_y/FA vary significantly with different ratios of MnO_x and FeO_x. It was found that the ratio of Mn⁴⁺/Mnⁿ⁺ first increased and then decreased, and the ratio of Mn³⁺/Mnⁿ⁺ slightly increased as the ratios of MnO_x and FeO_x increased. Mn_{0.15}Fe_{0.05}/FA has the highest ratio of Mn⁴⁺/Mnⁿ⁺ value (39.59%) and a high ratio of Mn³⁺/Mnⁿ⁺ (48.38%) within all samples. Among the catalysts, most of the Mn exists at high valence states (Mn³⁺, Mn⁴⁺), which is caused by the oxidation of lower valence state (Mn²⁺) contemporary leading to an electronic transfer, such as Mn⁴⁺ ↔ Mn³⁺ ↔ Mn²⁺. The order of the LTSCR activity from high to low is as follows: MnO₂ > Mn₅O₈ > Mn₂O₃ > Mn₃O₄ > MnO [30]. Furthermore, Mn has a high self-redox tendency leading to the formation of a large amount of higher valence state MnO_x [31]. Many studies have indicated that Mn⁴⁺ is the main factor in promoting the oxidation of NO to NO₂ during LTSCR. The co-existence of NO₂ and NH₃ in one circle can promote the LTSCR process through “fast reaction” [32]:

The Fe 2p spectra were deconvoluted into different valence states of Fe: Fe³⁺ (~725.1 and ~711.8 eV), Fe²⁺ (~723.5 and 710.1), and the satellite peak located at 718.5 eV [33]. Table 3 shows that most Fe species exist in the valence state of Fe³⁺. With the addition of MnO_x into Fe_{0.10}/FA, the ratio of Fe³⁺/Fe increased first and then decreased when the value of Mn/FA was higher than 0.15. However, when FeO_x was added to Mn_{0.15}/FA, the ratio of Fe³⁺/Fe also increased. This phenomenon indicates that the ratio of Mn/Fe is a critical factor in determining the catalytic capability of a catalyst during LTSCR reactions, and the optimum ratio of Mn/Fe could promote the cycle of redox as follows:

The transfer of electrons creates an unbalanced charge and underfilled chemical bonds, making it easier to produce oxygen vacancies and highly mobile oxygen. Highly mobile oxygen that is chemically adsorbed on the surface is one of the critical active species during the NH₃-SCR reaction [24].

The O 1s spectra were fitted with three sub-peaks [34]. The peak at ~529.9 eV represents the lattice oxygen (named as O_β). Defective metal-oxide (~531.4 eV) and chemisorbed water (~532.7 eV (OH^- or H_2O)) [35,36] are assigned to the chemically absorbed oxygen species on the surface (O_α). Table 3 shows that the chemically absorbed oxygen is the main form of oxygen species and is more reactive due to higher mobility, lower bonding energy to the surface, and a higher tendency to form NO_2 by oxidizing NO; which could promote “fast reaction” [37]. Furthermore, chemically adsorbed oxygen can activate oxygen gas [38], providing sufficient active oxygen species, ensuring fast recovery from low-state metal ion: $Mn^{3+} + 0.5O_2 \rightarrow Mn^{4+} + O^{2-}$, $Fe^{2+} + 0.5 O_2 \rightarrow Fe^{3+} + O^{2-}$ [39], which facilitate the excellent LTSCR.

Among all the synthesized catalysts, the active components within $Mn_{0.15}Fe_{0.05}/FA$ possess the lowest energy value (Table S1), caused by high electron cloud density. This phenomenon may have been caused by two factors: (i) The interaction between Mn and Fe could increase the redox cycle ability, which is significantly vital to activate the reactant; (ii) the co-existence of active metal species with a different state could provide unsaturated and unbalanced chemical bonds, which enhances NO_x removal [40]. $Mn_{0.15}Fe_{0.05}/FA$ also has a high ratio of O_α/O_t , acting as an active site for NH_3 adsorption to form. The high valence state metal (Mn^{4+} , Mn^{3+} and Fe^{3+}) provides active sites for the reactant adsorption and activation and promotes the redox cycle combined with active oxygen species explains the excellent NH_3 -SCR activity of $Mn_{0.15}Fe_{0.05}/FA$.

2.3.2. Reducibility for the Low-Temperature Activity

The existence of active species with different valence states within catalyst promotes the oxidation/reduction cycle proven by XPS results (Table 3). Thus, the redox property is an important index to evaluate the De- NO_x ability of the catalyst. The H_2 -TPR experiments were performed to examine the reducibility of different catalysts (Figure 2a,b). The H_2 -TPR curve of FA had a broad peak at around 400–650 °C, attributed to the reduction of FeO_x inherently present in FA [41]. When metal oxides were added, the intensity of this peak increased gradually and shifted to a higher temperature. This result is caused by electronic transfer and healthy interaction between metal oxides and carrier, as indicated by XRD results that the metal oxide was doped into the SiO_2 crystal structure. $Fe_{0.10}/FA$ produced two main peaks at around 419 and 572 °C that were associated with the reduction of Fe_2O_3 to Fe_3O_4 , and Fe_3O_4 to FeO [41], respectively. Three peaks ((α) 332, (β) 429, and (δ) 488 °C) appeared in $Mn_{0.15}/FA$ curve (Figure 2b), responsible for the reduction of the manganese oxide species [42]. All bimetal oxides containing catalysts produced peaks in three zones and were denoted as α , β , and δ , respectively. Based on a previous study [43], these zones were assigned to $MnO_2 \rightarrow Mn_2O_3$ (α), $Mn_2O_3 \rightarrow Mn_3O_4$, $Fe_2O_3 \rightarrow Fe_3O_4$ (β), $Mn_3O_4 \rightarrow MnO$, and $Fe_3O_4 \rightarrow FeO$ (δ).

The primary objective of this work is to understand the reducibility of NO_x by the catalysts at lower temperatures. Therefore, the first two zones were considered (Figure 2a,b). Furthermore, semi-quantitative H_2 -TPR analysis was conducted by calculating the peak area, and the results are given in Figure 3. For Mn_xFe_y/FA , the onset of reduction shifts to lower temperatures increasing the peak area of all peaks with the addition of MnO_x or FeO_x . This phenomenon is caused by the interaction of MnO_x , FeO_x , and the carrier within the catalysts. Figure 3 shows that with the increase in MnO_x or FeO_x concentration, the peak area responsible for low-temperature reducibility (α) gradually increased. $Mn_{0.15}Fe_{0.10}/FA$ and $Mn_{0.15}Fe_{0.05}/FA$ have the best De- NO_x activity within the series of the $Mn_xFe_{0.10}/FA$ and the $Mn_{0.15}Fe_y/FA$, respectively. These two catalysts have medium reducibility. Therefore, the medium reducibility of $Mn_{0.15}Fe_{0.05}/FA$ is an essential factor contributing to its outstanding De- NO_x activity.

Generally, the adsorption of gas reactants is the first step for a gas-solid reaction. Furthermore, SCR reactions are well established to be involved in both redox and adsorption active sites. To examine the NH_3 and NO adsorption and activation ability of the catalyst, temperature program desorption, in-situ DRIFTS, and TG-MS techniques were used.

Figure 2. Profiles of H_2 -TPR (a), NH_3 -TPD (c), and NO-TPD (e) of $Mn_xFe_{0.10}/FA$ ($x = 0, 0.05, 0.15$ and 0.20); and H_2 -TPR (b), NH_3 -TPD (d), and NO-TPD profiles (f) of $Mn_{0.15}Fe_y/FA$ ($y = 0, 0.05$ and 0.10).

Figure 3. The peak area of NO/NH₃-TPD and H₂-TPR on different catalysts.

2.3.3. The Adsorption and Desorption Behavior of NH₃/NO

The surface acid property of the catalyst is highly essential for NH₃ adsorption on acidic sites. This is the first step of the NH₃-SCR reaction. Thus, the strength and number of acidic sites were calculated by NH₃-TPD technology. Figure 2c,d shows that all the NH₃ desorption profiles showed one broad peak, including two desorption processes [44]: (1) NH₃ desorption by weak acid sites (100–200 °C) and (2) NH₃ desorption peak (200–400 °C) attributed to medium acid sites. The peak area allows for a semi-quantitative understanding of acid sites, and the results are shown in Figure 3. The carrier can provide a small number of acid sites because FeO_x is inherently present in FA. For all catalysts, the total acidic sites of Fe_{0.10}/FA is the lowest but is the highest for Mn_{0.15}/FA. However, bimetal-containing catalysts have similar total acidic sites. Mn_{0.15}Fe_{0.05}/FA has a slightly lower number of weak acidic sites, but it has the highest de-NO_x activity. It can be concluded from this result that mediocre surface acid property is just one of the factors influencing De-NO_x activity because excess and heavy adsorption of NH₃ could have an inhibitory effect for De-NO_x efficiency [45].

Figure 2e,f shows the temperature-programmed desorption of NO_x to test the adsorption capacity of NO. All samples present a broad desorption peak at the temperature range of 50–400 °C. This temperature range can be divided into two segments: (1) At temperatures lower than 250 °C which is the desorption of physisorbed NO and disintegration of unstable nitrite species occurs, and (2) temperatures higher than 250 °C represents NO₂ desorption due to the decomposition of stable thermal nitrates, such as bridged nitrate or bidentate bitrate that have high thermal stability [39]. The area of desorption peak could represent the semi-quantitative amount of NO_x species, and the results are shown in Figure 3. For all catalysts, the desorption amount of NO and NO₂ increased with MnO_x addition. In contrast, the desorption amount of NO increased and then decreased as the concentration of FeO_x increased; the desorption amount of NO₂ increased continuously. Therefore, it can be concluded that the balance between the adsorption of reactants (NH₃ and NO_x) and the redox ability of metal oxide plays a significant role in LTSCR.

To further investigate the decomposition characteristics of surface adsorbed species over Mn_{0.15}Fe_{0.05}/FA, the pre-adsorbed catalyst with NH₃ was studied with TG-MS (Figure S5). TG thermograms (Figure S5a) show a slight weight loss caused merely by the desorption of gas because the sample was calcinated at 500 °C for 3 h. Mn_{0.15}Fe_{0.05}/FA can readily adsorb NH₃ at 50 °C,

and then release NH_3 species during the entire heating process, including NH_3 , NH_2 , NH_4^+ , and N_2O . When the temperature increased, the NH_3 was released. Because some of the NH_3 was physically adsorbed and/or weakly chemically adsorbed on the Lewis acid sites, nevertheless, some ammonia species are chemically adsorbed on the active sites of $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ and can be activated by surface oxygen, such as surface oxygen, which can dehydrogenate NH_3 and form intermediate surface species ($-\text{NH}_2$) [46]. The activated amide ($-\text{NH}_2$) groups have been a critical intermediate species because they can react with activated NO to form NH_2NO , which further decomposes to form N_2 and H_2O , favoring the conversion of NO_x [47]. NH_4^+ was formed by chemically adsorbed NH_3 on the Brønsted acid sites. The results also showed that the formation of N_2O due to the side reaction ($4\text{NH}_3 + 4\text{O}_2 \rightarrow 2\text{N}_2\text{O} + 6\text{H}_2\text{O}$). The formation of a large amount of N_2O at 250°C is the most important factor limiting the De- NO_x capability of $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ at this temperature. All of the activated ammonia species act as an excellent intermediate during the SCR process [48].

Figure S6a shows the result of a mass change of pre-adsorbed NO on $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$, and the desorbed species were recorded by TG-MS (Figure S6b–d), such as H_2O , NO , and NO_2 . The TG thermogram (Figure S6a) shows two weight loss stages. The first stage at around 100°C was assigned to dehydration and was recorded by MS (Figure S6b). The NO was released during all the weight loss stages, which the weakly adsorbed NO was released on the catalyst surface (Figure S6c). NO_2 was disorbed in the second stage (Figure S6d), which was caused by gaseous NO reacting with the surface chemical oxygen to produce NO_2 over Fe^{n+} and Mn^{n+} sites at a lower temperature [25,49], and promotes the De- NO_x activity by “fast reaction”. This reaction pathway is one of the reasons $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ has an excellent low-temperature activity.

2.3.4. In-Situ DRIFT Analysis

SCR catalytic performance is highly dependent on the adsorption capability of the catalyst. Gases such as O_2 , NO , and NH_3 are primary participants during SCR reaction. The adsorption capability of the catalyst was discussed in detail in the previous section. However, it is essential to understand the reactions occurring on the surface of the catalyst after the adsorption of primary participants. To understand the mechanism of the reactions on the surface of $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ catalyst by adsorption and reaction of reactants at active sites, the intermediates, and adsorbed species, four different experiments were conducted using the in-situ DRIFT at 150°C : (1) NH_3 adsorption; (2) $\text{NO} + \text{O}_2$ adsorption; (3) the reaction of $\text{NO} + \text{O}_2$ with pre-adsorbed NH_3 ; and (4) the reaction of NH_3 with pre-adsorbed $\text{NO} + \text{O}_2$.

The NH_3 adsorption spectra are given in Figure 4a. Several peaks appeared immediately when the NH_3 was introduced into the reaction cell after 1 min, such as 1621 , 1405 , 1349 , 1229 , 966 , and 929 cm^{-1} . This phenomenon shows that $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ catalyst has a strong surface acidity, which can make NH_3 readily adsorbed and then facilitate the De- NO_x reaction. During the 30 min adsorption of NH_3 , many adsorption peaks gradually increased in intensity. Studies show that these peaks can be divided into four groups: (1) The strong bands centered at 1621 , 1270 , 1227 , and 1086 cm^{-1} were assigned to symmetric-asymmetric bending vibrations of the N–H bonds within NH_3 coordinately associated with Lewis acid sites [50]; (2) the 1694 and 1405 cm^{-1} weak bands were attributed to the N–H bending vibration of NH_4^+ species on Brønsted acid sites [51]; (3) the two bands at 1530 and 1349 cm^{-1} can represent $-\text{NH}_2$ species [52], which were formed by the intermediate oxidation of adsorbed ammonia species. From the results of Figure S5, the formation of the activated amide ($-\text{NH}_2$) groups from dehydrogenation of NH_3 is evident [46]; (4) the groups centered at 966 and 929 cm^{-1} were assigned to loosely adsorbed NH_3 [44], indicating that NH_3 can be readily adsorbed and activated on $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$.

Figure 4. In-situ DRIFT spectra of NH_3 adsorption over the $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ exposed to (a) 1000 ppm NH_3/N_2 and (b) 1000 ppm $\text{NO} + 5\% \text{O}_2$ at 150°C .

Figure 4b shows the in-situ DRIFT spectra of $\text{NO} + \text{O}_2$ adsorption on $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$. A series of adsorption peaks (1627 , 1438 , 1379 , 1337 , and 1274 cm^{-1}) appeared in the first minute when the mixed gas was added into the reaction cell. The reactant ($\text{NO} + \text{O}_2$) can be readily adsorbed on the catalyst surface and then facilitate the De- NO_x reaction. The intensity of the adsorption peaks increased with time, indicating that the catalyst has a high adsorption ability of reactant. The high adsorption ability of the catalyst allows for an efficient SCR reaction, explaining the excellent catalytic performance of $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$. The asymmetric stretching vibration of loosely adsorbed NO_2 was shown at 1627 cm^{-1} [53], formed as a result of NO reacting with O_2 and/or the reaction of NO and chemisorbed oxygen [54]. The bands at 1438 , 1337 , and 1274 cm^{-1} were assigned to bridged nitrate, monodentate nitrate, and bidentate nitrate [54]. The bands at 1379 and 1048 cm^{-1} are responsible for trans- and cis- $\text{N}_2\text{O}_2^{2-}$ [47]. When the pre-adsorbed ($\text{NO} + \text{O}_2$) catalyst was purged by nitrogen, most of the peaks appeared weaker than before, indicating that the adsorbed NO_x species are easily formed and decomposed, facilitating the cycle of nitro compounds, making a good foundation on the reaction.

The in-situ DRIFT spectra of the reaction between $\text{NO} + \text{O}_2$ and pre-adsorbed NH_3 at different time intervals are shown in Figure 5a. As mentioned above in (Figure 4a), after the adsorption of NH_3 , the catalyst exhibits Lewis (L) acid sites related bands (1621 , 1269 , 1227 , and 1086 cm^{-1}), Brønsted (B) acid sites (1694 and 1405 cm^{-1}), loosely adsorbed NH_3 (966 and 929 cm^{-1}) and $-\text{NH}_2$ (1530 and 1349 cm^{-1}). When $\text{NO} + \text{O}_2$ mixture was introduced, both the acid sites (L and B) and active intermediate bands decreased immediately, and many new nitrate species bands appeared and increased gradually during the reaction process. These changes indicated that almost all of the adsorbed NH_3 species could react with $\text{NO} + \text{O}_2$ to form new species, such as bridged nitrate (1616 cm^{-1}), bidentate nitrate (1696 , 1568 , 1270 , and 1102 cm^{-1}) [55], monodentate nitrate (1355 cm^{-1}), trans- and cis- $\text{N}_2\text{O}_2^{2-}$ (1403 and 1031 cm^{-1}), unstable nitrate species (1227 cm^{-1}) [56]. Over time, these peaks became more pronounced. However, the intensity of loosely adsorbed NH_3 (967 and 929 cm^{-1}) slightly decreased, which indicates that it reacted with NO_x species and formed a small number of nitrate species.

The other transient reaction experiment was also carried out. In this reaction, $\text{NO} + \text{O}_2$ was co-adsorbed at first, and then NH_3 was added. The results are given in Figure 5b. As observed, before the addition of NH_3 , the bands of NO_x species (NO_2 (1627 cm^{-1}), bridged nitrate (1438 cm^{-1}), monodentate nitrate (1337 cm^{-1}), bidentate nitrate (1274 cm^{-1}), trans- and cis- $\text{N}_2\text{O}_2^{2-}$ (1379 and 1048 cm^{-1})) were identical to the previous experiment shown in Figure 5b. After the addition of NH_3 , the following phenomena were observed: (1) the intensity of the peak assigned to the adsorbed NO_2 (NO oxidation by active oxygen-species) and nitrate species decreased immediately; (2) some of the NH_3 species (NH_3 coordinate to Lewis acid sites (1085 cm^{-1}), trans- $\text{N}_2\text{O}_2^{2-}$ (1379 cm^{-1}) and loosely

adsorbed NH_3 (967 and 929 cm^{-1})) appeared, and the intensity increased with time; (3) formation of new nitrate species such as bridged nitrate (1617, 1458 cm^{-1}), bidentate nitrate (1568 and 1538 cm^{-1}), monodentate nitrate (1337 cm^{-1}), unstable nitrate species (1242 cm^{-1}) and trans- $\text{N}_2\text{O}_2^{2-}$ (1379 cm^{-1}). Among these, the bands of monodentate nitrates (1337 cm^{-1}) were always present and increased with time, suggesting that the monodentate nitrates did not react with ammonia species, and the other NO_x species (bidentate nitrate and trans- $\text{N}_2\text{O}_2^{2-}$) reacted with NH_3 to form monodentate nitrates. However, the bands of weakly adsorbed NO_2 (1627 cm^{-1}), bidentate nitrate (1274 cm^{-1}) and cis- $\text{N}_2\text{O}_2^{2-}$ (1048 cm^{-1}) quickly vanished, indicating that they reacted with the introduced NH_3 .

Figure 5. In-situ DRIFT spectra of (a) $\text{NO} + \text{O}_2$ reacted with pre-adsorbed NH_3 , and (b) NH_3 reacted with pre-adsorbed $\text{NO} + \text{O}_2$ over the $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ at 150 °C.

2.3.5. Mechanisms and Reaction Pathways

NH_3/NO -TPD and pre-adsorbed NH_3/NO -TG-MS results showed that $\text{Mn}_{0.15}\text{Fe}_{0.05}/\text{FA}$ could quickly adsorb and activate the reactants at 150 °C, which is promoted by the addition of a proper amount of metal ion providing the optimum amount of acid and active sites. The primary function of active sites is to adsorb and activate the reactants (NH_3 , NO_x , and O_2) to produce the NH_3 species and nitrates. Moreover, in-situ DRIFTS analysis showed that NH_3 could be easily oxidized to NH_2 as an active intermediate were adsorbed on Lewis and Brønsted acid sites. With the introduction of $\text{NO} + \text{O}_2$, most of the adsorbed ammonia species decreased, and new species were formed (Figure 5a). The highly reactive NH_2 species reacted with NO_x (NO , NO_2) to form NH_2NO or NH_2NO_2 , which rapidly decomposed into N_2 and H_2O [57]. As given in Figure 5b, the adsorbed NO_2 or nitrates species reacts with adsorbed ammonia species when the NH_3 was confirmed to follow the Langmuir–Hishelwood (L–H) mechanism.

According to several previous studies [58] combined with our findings, the L–H reaction pathway mainly occurs during the reaction as follows: (M denotes Fe and/or elemental Mn)

3. Materials and Methodology

3.1. Preparation of Catalysts

The catalyst samples were obtained by a co-impregnation technique using FA as the catalyst carrier. The FA used in this study was obtained from Fushun Zhong Ji Thermal Power Plant, Fushun, China. The elemental composition of FA consists of SiO₂ (47.42%), Al₂O₃ (24.25 wt.%), Fe₂O₃ (7.91 wt.%), CaO (3.44 wt.%), TiO₂ (1.89 wt.%), K₂O (1.74 wt.%), MgO (1.12 wt.%), and others (measured by X-ray fluorescence analysis). The FA was dried at 105 °C for 12 h before all experiments. Fe(NO₃)₃·9H₂O (99.99%, AR) and Mn(NO₃)₃·4H₂O (99.99%, AR) were used as precursors, and they were obtained from Sinopharm Chemical Reagent Co. Ltd, (Shanghai, China).

The catalysts were prepared in the following order: Firstly, a different concentration of manganese nitrate and iron nitrate was dissolved in de-ionized water. Secondly, 4 g of FA was added to the solution with the ultrasonication of the slurry for 1 h at 80 °C. Thirdly, aqueous ammonia solution (75%) (Sinopharm Chemical Reagent Co. Ltd, (Shanghai, China)) was added drop by drop until a basic mixture was obtained (pH ~ 10). Then, the mixture was dried at 105 °C for 10 h prior to the calcination process. The catalyst sample was calcined in an electric oven at 500 °C at 10 °C/min for three hours. After that, the dried product with a particle size range of 250–400 µm was used for further analysis. The obtained samples were named Mn_xFe_y/FA, in which the value of 'x' ranges from 0 to 0.2, and the value of 'y' ranges from 0 to 0.10, representing the weight ratios of manganese/FA and iron/FA, respectively. For comparison purposes, fly ash was treated via the same preparation method, named FA.

3.2. Low-Temperature SCR Experiments

The NH₃-SCR activity was conducted in a fixed-bed quartz reactor (20 mm i.d.). The experimental setup (Figure 6) consists of three parts: the flue gas simulation system, reaction system, and tail gas test system. The reaction was conducted under a mixture of gases (with (NO) and (NH₃) of 0.1 vol.%, and (O₂) of 5 vol.%), and N₂ (1200 mL·min⁻¹) was used as a balance gas, equivalent to a GHSV of 50,000 h⁻¹. Activity tests were carried out each 50 °C in the range of 100 to 300 °C, which was heated using a tubular furnace. The concentration of NO_x (NO and NO₂) was measured by a flue gas analyzer (MRU 5, Germany) and were recorded at each test temperature after stabilization for half an hour.

NO_x conversion is calculated by Equation (14).

$$\text{NO}_x \text{ Conversion (\%)} = \frac{C_{\text{NO}_x \text{ in}} - C_{\text{NO}_x \text{ out}}}{C_{\text{NO}_x \text{ in}}} \times 100\% \quad (14)$$

where C_{NO_x in} and C_{NO_x out} are the NO_x concentration at the reactor inlet and outlet, respectively.

3.3. Characterization of Catalyst Samples

The morphology of the materials was analyzed by scanning electron microscopy (SEM, Zeiss SIGMA HD, (Oberkochen, Germany)). The physical properties of the catalysts were checked by an N₂-physisorption analyzer using Kubo X1000 (Beijing Builder Electronic Technology Co. LTD, (Beijing, China)). The X-ray diffraction patterns were determined (Ultima IV, Rigaku, (Tokyo, Japan)) using a Cu K^α radiation to obtain the crystal phase structure. The composition of Fe and Mn within the catalysts were determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) technique, using Horiba Ultima 2 (Horiba, LTD, (Kyoto, Japan)). A high-performance

electron spectrometer (ESCALAB 250, Thermo Fisher Scientific, Inc., (Waltham, MA, USA)) was used to carry out the X-ray photoelectron spectroscopy (XPS) experiments with monochromatic Al $K\alpha$ radiation (1486.8 eV, 150 w) and the C 1s (284.8 eV) as a reference to calculate the binding energies to investigate the elemental state of catalyst surfaces. The XPS peak 4.1 software was used for curve fitting (Shirley background, Gaussian-Lorentzian ratio fixed to 80/20).

Figure 6. The schematic diagram of the experimental setup for De-NO_x experiments.

The temperature-programmed desorption (NH₃/NO-TPD) and the temperature program reduction (H₂-TPR) experiments were conducted on the chemisorption analyzer with a TCD (PCA-1200, Beijing Builder Electronic Technology Co. LTD (Beijing, China)). Before each TPD experiment, all the samples were de-gassed in He (30 mL·min⁻¹) at 300 °C for 1 h. The absorption segment was carried out in 10 vol.% NH₃/He (or 10 vol.% NO/He) at 50 °C for 1 h, and then the samples were purged by He for half an hour to reach a stable baseline. Finally, the temperature of the catalyst was increased to 400 °C (10 °C·min⁻¹). However, the H₂-TPR experiment started with a stable baseline by TCD under H₂ flow (10 vol.% H₂/Ar). Then, the TCD test was carried out during the heating of the catalyst to 800 °C (10 °C·min⁻¹). Desorption and decomposition properties of the surface species of the catalyst were tested by a simultaneous thermal analyzer (STA 8000, PerkinElmer, Inc., (Waltham, MA, USA)) attached with a Hiden HPR20 mass spectrometer (MS) (Hiden Analytical, Inc., (Peterborough, NH, USA)). Before each run, the sample was first adsorbed with NO or NH₃, similar to the TPD process. Then, the temperature was ramped at a similar heating rate (10 °C·min⁻¹) under helium. The in-situ DRIFT spectroscopy was conducted on FTIR spectrometer (Nicolet IS50, Thermo Fisher Scientific, Inc., (Waltham, MA, USA)) equipped with a ZnSe reaction cell. The sample was first de-gassed at 300 °C for 1 h under nitrogen gas (100 mL·min⁻¹) to remove any adsorbed species (e.g., air or vapor). During the experiment, the background spectrum was obtained at the corresponding temperature, and then the reactant gas ([NH₃] = 1000 ppm or [NO] = 1000 ppm combine with [O₂] = 5 vol.%) was introduced.

4. Conclusions

The Mn_{0.15}Fe_{0.05}/FA catalysts supported on coal fly ash had an excellent LTSCR catalytic performance in the temperature window between 130 °C and 300 °C. The optimum SCR activity in this study was obtained in the catalyst containing 0.05 and 0.15 weight ratios of Mn/FA and Fe/FA, respectively.

The great De-NO_x activity of Mn_{0.15}Fe_{0.05}/FA was attributed to the following favorable properties: (1) The doped FeO_x can promote the production of more high valence states of Mn that enriched these

Mn⁴⁺ species on the surface; (2) the interaction between the doped species (MnO_x, FeO_x) and FA provides an abundant amount of active sites, promoting adsorption and activation of reactants; (3) the proper amount of acid property, reactant adsorption, and redox ability together are the primary factors contributing to the excellent LTSCR efficiency for Mn_{0.15}Fe_{0.05}/FA; (4) the synthesis of Mn_{0.15}Fe_{0.05}/FA provides a potential high value-added application of coal fly ash, not only to decrease NO_x emissions but also to promote the development of cost-effective low-temperature NH₃-SCR catalysts.

The presence of SO₂ (even in a small amount) may strongly impact the performance of low-temperature SCR systems. Future research should be focused on improving the SO₂ poisoning resistance of the catalysts by introducing additives and changing the structure of catalysts.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/12/1399/s1>, Figure S1: The SEM images of (a) FA, (b) Fe_{0.10}/FA, (c) Mn_{0.05}Fe_{0.10}/FA, (d) Mn_{0.15}Fe_{0.10}/FA, (e) Mn_{0.20}Fe_{0.10}/FA, (f) Mn_{0.15}/FA and (g) Mn_{0.15}Fe_{0.05}/FA; Figure S2: N₂ adsorption-desorption isotherms and pore size distribution plots of different catalyst samples; Figure S3: XRD patterns of different catalysts samples: (a) Mn_xFe_{0.10}/FA (x=0, 0.05, 0.15, and 0.20) and (b) Mn_{0.15}Fe_y/FA (y=0, 0.05, and 0.10); Figure S4: The XPS spectra of (a) Mn 2p spectra, (b) Fe 3p spectra, (c) O 1s over different catalysts, respectively; Figure S5: TG and DTG curves (a) and mass spectra of nitrogen-containing species (b)–(e) during the heating of the Mn_{0.15}Fe_{0.05}/FA catalyst that pre-adsorbed NH₃; Figure S6: TG and DTG curves (a) and mass spectra of nitrogen-containing species (b)–(e) during the heating of the Mn_{0.15}Fe_{0.05}/FA catalyst that pre-adsorbed NO; Table S1: The results of XPS analyses of the catalysts.

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