

Article

Promoting Effect of Ti Species in MnO_x-FeO_x/Silicalite-1 for the Low-Temperature NH₃-SCR Reaction

Jialiang Gu ¹, Rudi Duan ¹, Weibin Chen ¹, Yan Chen ², Lili Liu ¹ and Xidong Wang ^{1,*}

¹ Beijing Key Laboratory for Solid Waste Utilization and Management, Department of Energy and Resources Engineering, College of Engineering, Peking University, Beijing 100871, China; jialiang_gu@pku.edu.cn (J.G.); duanrudi912@163.com (R.D.); chenwb@pku.edu.cn (W.C.); liu-0806@163.com (L.L.)

² State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China; ychen1990@126.com

* Correspondence: xidong@pku.edu.cn; Tel.: +86-10-8252-9083

Received: 28 April 2020; Accepted: 13 May 2020; Published: 19 May 2020



Abstract: Manganese and iron oxides catalysts supported on silicalite-1 and titanium silicalite-1 (TS-1) are synthesized by the wet impregnation method for the selective catalytic reduction (SCR) of NO_x with NH₃ (NH₃-SCR), respectively. The optimized catalyst demonstrates an increased NO_x conversion efficiency of 20% below 150 °C, with a space velocity of 18,000 h⁻¹, which can be attributed to the incorporation of Ti species. The presence of Ti species enhances surface acidity and redox ability of the catalyst without changing the structure of supporter. Moreover, further researches based on in situ NH₃ adsorption reveal that Lewis acid sites linked to Mn⁴⁺ on the surface have a huge influence on the improvement of denitration efficiency of the catalyst at low temperatures.

Keywords: denitration; silicalite-1; titanium; NH₃-SCR

1. Introduction

Nitrogen oxides (NO_x) bring out a series of environmental problems, such as photochemical pollution, acid rain and haze, which seriously threaten human health [1,2]. Nowadays, selective catalytic reduction (SCR) with NH₃ has been proved to be an effective technology for NO_x emission control, which has been widely used in coal-fired power plants [3–5]. Commercial V₂O₅-WO₃/TiO₂ catalysts are very suitable for power plants, mainly due to the flue gas there, with a high temperature (>300 °C), which can satisfy the required reaction temperature of the catalyst. However, there are still a large number of untreated NO_x derived from industrial activities such as cement kilns, steel sintering and waste incinerators, where the temperature of flue gas is too low (<200 °C) to suit for these commercial catalysts [6,7]. Therefore, it is urgent to develop novel high-efficient catalysts, which have high catalytic activities at low temperatures.

Manganese-based catalysts are proved to be excellent denitration catalysts at low temperatures among the commonly used transition metal oxide catalysts [8–10]. Furthermore, numerous metals, like Fe, Ce and Cu, are used as active components to modify manganese-based catalysts, and for that purpose, the single manganese oxides can only maintain high denitrification activities in a narrow temperature window, accompanied by several side reactions [11–14]. In addition, proper supporters can not only provide a huge surface to disperse the active components, but can also supply abundant adsorption sites for the heterogeneous reactions [15,16]. Both Al₂O₃ and TiO₂ have been widely investigated as common supporters in the last few decades. However, the limited specific surface area, as well as poor water and sulfur resistance of the catalysts, hinder their further developments in industrial applications [17,18]. At the same time, carbon-based materials are also

applied as supporters of catalysts, because of their large surface area, unique porous structure and abundant oxygen functional groups. Nevertheless, the poor thermal stability and oxidizability of carbon-based materials are a potential safety hazard in industrial applications [19–21]. In recent years, zeolites have gained widespread attention as supporters in SCR studies, due to their high thermal stability, unique porous structure and absence of harmful substances [22–24]. Wang et al. [25] found that the optimized Mn-Fe/ZSM achieved 100% NO_x conversion efficiencies from 150 °C to 250 °C. The excellent catalytic performance can be attributed to the addition of iron, which increases the levels of Mn⁴⁺ and oxygen vacancy. Nevertheless, the presence of Al species in ZSM-5 makes contributions to its strong hydrophilicity, which hinders its applications in industrial denitration, because the flue gas is usually humid. However, silicalite-1 is reported to exhibit excellent water resistance in an NH₃-SCR reaction, which can be attributed to the decrease in hydrophilicity due to the absence of heteroatoms [26,27]. However, compared with ZSM-5, the surface acidity of silicalite-1 is a little bit weaker, which is the key to the low-temperature denitration. To date, Ti atoms have been reported to replace a small amount of Si atoms for improving the surface acidity and maintaining excellent water resistance, which can benefit the low-temperature denitration [28].

Herein, we introduce novel high-efficient denitration catalysts with highly dispersed MnO_x and FeO_x nanoparticles supported on silicalite-1 and titanium silicalite-1 (TS-1) respectively. Compared to the catalyst supported on silicalite-1, the catalyst supported on TS-1 demonstrates superior NO_x conversion efficiencies in the NH₃-SCR reaction at low temperatures, which can be attributed to the incorporation of Ti species, without changing the structure of zeolites. Moreover, further researches on the surface properties of catalysts including their acidity, redox ability and in-situ adsorption, reveal that the presence of Ti species promotes the formation of Mn⁴⁺ on the surface, thereby increasing the acidity and redox ability of the catalyst, which are beneficial for the low-temperature denitration.

2. Results and Discussion

2.1. Chemical Compositions and Textural Properties of Samples

The chemical compositions of the catalysts are summarized in Table 1, based on the results of ICP-OES. The mass ratios of active metal oxides are close to the initial feed ratios. The contents of Mn and Fe species make no significant difference among all the catalysts.

Table 1. Chemical compositions of samples.

| Sample | The Mass Fraction of Metal Elements/wt.% | | |
|---|--|------|------|
| | Mn | Fe | Ti |
| Mn ₃ Fe ₂ /Silicalite-1 | 3.18 | 1.87 | - |
| Mn ₃ Fe ₂ /TS-1-30 | 3.17 | 1.97 | 2.23 |
| Mn ₃ Fe ₂ /TS-1-20 | 3.11 | 1.94 | 3.56 |

The X-ray diffraction (XRD) patterns of the supporters are shown in Figure 1a. All of the supporters display obvious characteristic peaks at 7.9°, 8.8°, 23.1°, 23.8° and 24.3°, which can be attributed to a typical Mobil Five Instructure (MFI) structure. The pattern of anatase at 25.4° does not appear in TS-1-30, while it is found in TS-1-20, which indicates that the excessive Ti species form a small amount of anatase in TS-1-20. The existing form of Ti species in the supporters is further confirmed by Fourier transform infrared (FT-IR). As shown in Figure 2, the bands at 433, 545–546, 799–803, 1074–1075 and 1223–1225 cm⁻¹ can be assigned to the characteristic peaks of MFI structure; the bands at 957–958 cm⁻¹ can be the evidence for the incorporation of Ti species into frameworks [29]. Moreover, it can be seen from Figure 1b that there is no peak relevant to metal oxides in the supported catalysts, due to the extremely low metal loading of the catalysts. However, all the supported catalysts possess clear peaks that are consistent with corresponded supporters, which reveals that the supported catalysts remain the same structure with the supporters after the impregnation process [25,30].

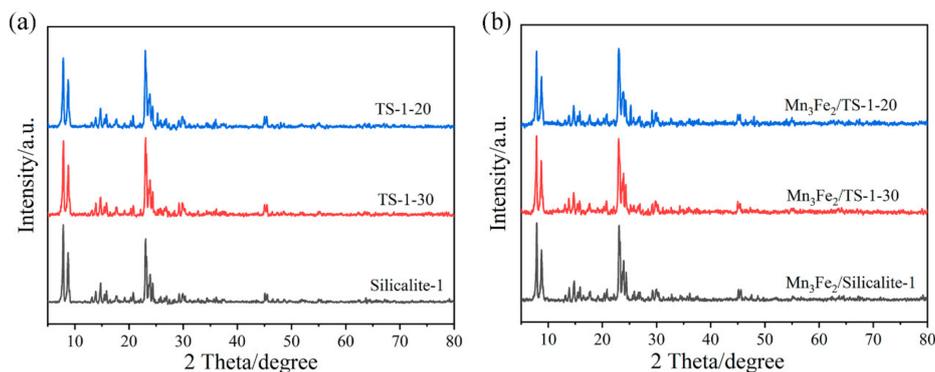


Figure 1. X-ray diffraction (XRD) patterns of supports (a) and catalysts (b).

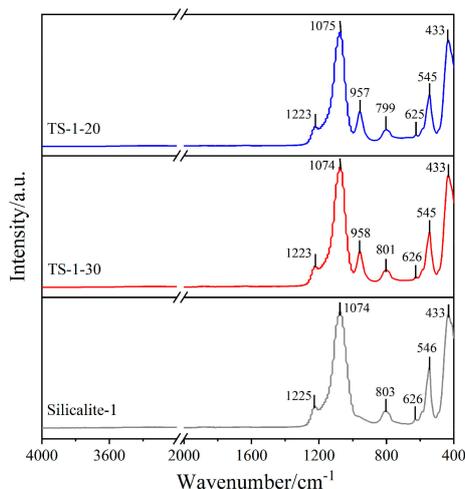


Figure 2. Fourier transform infrared (FT-IR) spectra of supports.

N₂ adsorption/desorption isotherms of the samples are illustrated in Figure 3, and the corresponding textural properties of the samples are summarized in Table 2. The isotherms can be classified as type I, indicating that all the samples have microporous structures [31,32]. The specific surface area, total pore volume and average pore diameter of Silicalite-1 are 454.31 m²/g, 0.32 cm³/g and 2.85 nm, respectively. When Ti species are introduced into the structure of zeolites, both TS-1-30 and TS-1-20 show an increase of 10% in specific surface area, total pore volume and average pore diameter, which can be attributed to the difference of atom size between Ti and Si [29]. After loading MnO_x and FeO_x, both specific surface area and total pore volume have a decrease of 10%, while average pore diameter remains constant, indicating that most of MnO_x and FeO_x species coexist on the surface, without changing the textural properties of supports, as proposed in XRD analysis [30].

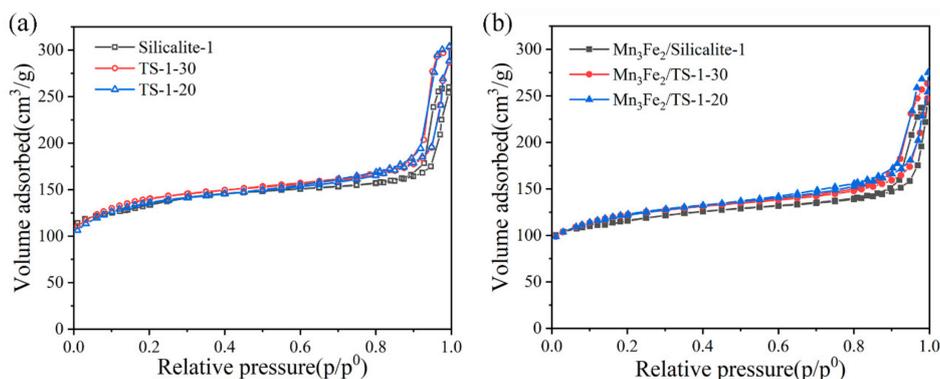


Figure 3. N₂ adsorption/desorption isotherm of supports (a) and catalysts (b).

Table 2. Textural data of samples.

| Sample | BET Surface Area (m ² /g) | Pore Volume (cm ³ /g) | Pore Diameter (nm) |
|---|--------------------------------------|----------------------------------|--------------------|
| Silicalite-1 | 454.31 | 0.32 | 2.85 |
| TS-1-30 | 485.43 | 0.37 | 3.08 |
| TS-1-20 | 471.39 | 0.37 | 3.16 |
| Mn ₃ Fe ₂ /Silicalite-1 | 393.64 | 0.27 | 2.76 |
| Mn ₃ Fe ₂ /TS-1-30 | 422.14 | 0.32 | 3.08 |
| Mn ₃ Fe ₂ /TS-1-20 | 423.22 | 0.31 | 2.96 |

The morphologies of the catalysts are further investigated by SEM and transmission electron microscopy (TEM), with the results illustrated in Figure 4. The SEM images of catalysts present a typical MFI structure with a particle size of about 150 nm. However, the incorporation of Ti species results in some nanoscale folds on the surface of the catalysts, which can be attributed to the difference of atom size between Ti and Si. The active metal oxides are highly dispersed on the surface of catalysts in the form of small particles from the TEM images. As shown in Figure 5, the element mapping by energy-disperse X-ray spectroscopy (EDS) is applied to further identify the compositions of these small particles on the surface of the catalysts (EDS mappings of the supporters are shown in Figure S1). It can be found from Figure 5 that Mn, Fe and Ti species are all uniformly dispersed around the supporters. Besides, the results of Mn and Fe species are similar, indicating that Mn and Fe species may coexist in the form of FeMnO_x, due to a strong interaction between metal oxides [33–35]. In summary, the introduction of Ti species does not change the textural properties of catalysts, but the surface of the catalysts is wrinkled, due to the difference of atom size between Ti and Si, which may provide better active sites for the catalytic reaction.

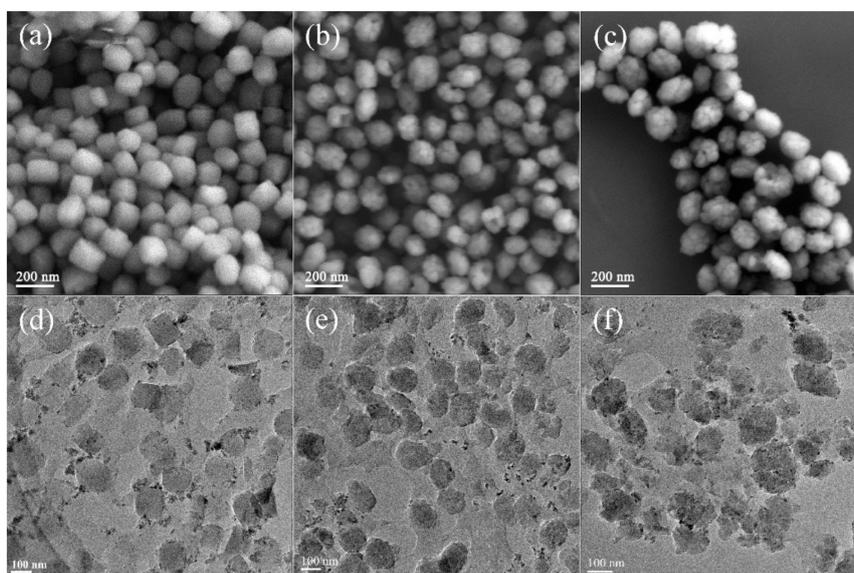


Figure 4. SEM and transmission electron microscopy (TEM) images of catalysts: (a,d) Mn₃Fe₂/Silicalite-1; (b,e) Mn₃Fe₂/TS-1-30; (c,f) Mn₃Fe₂/TS-1-20.

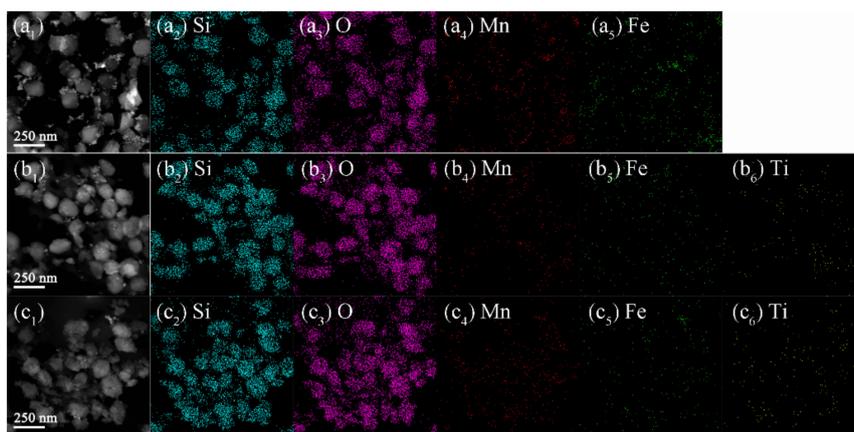


Figure 5. STEM images and energy-disperse X-ray spectroscopy (EDS) mappings of catalysts: (a) $\text{Mn}_3\text{Fe}_2/\text{Silicalite-1}$; (b) $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$; (c) $\text{Mn}_3\text{Fe}_2/\text{TS-1-20}$.

2.2. Surface Constituent and Chemical States of Samples

Figure 6 displays the XPS spectra of Mn 2p, Fe 2p and O 1s for different catalysts, and the results are summarized in Table 3. It can be seen from Figure 6a that the Mn 2p spectra consist of two major peaks that are assigned to Mn $2p_{3/2}$ (peak around 642 eV) and $2p_{1/2}$ (peak around 654 eV). The Mn $2p_{3/2}$ peak can be fitted by three peaks (around 642 eV, 643 eV and 645 eV), which can be assigned to Mn^{2+} , Mn^{3+} and Mn^{4+} , respectively [36,37]. Figure 6b displays the spectra of Fe 2p, which contains two main peaks relevant to Fe $2p_{3/2}$ (peak around 710 eV) and $2p_{1/2}$ (peak around 725 eV). The Fe $2p_{3/2}$ can be separated into two independent peaks (around 713 eV, 710.7 eV), which can be assigned to Fe^{2+} and Fe^{3+} [13,38,39]. Regarding the oxygen species, O 1s spectra are shown in Figure 6c. The spectra can be separated into two peaks that related to the lattice oxygen (peak around 530 eV, labeled as O_α) and surface adsorbed oxygen (peak around 533 eV, labeled as O_β) [40,41], respectively.

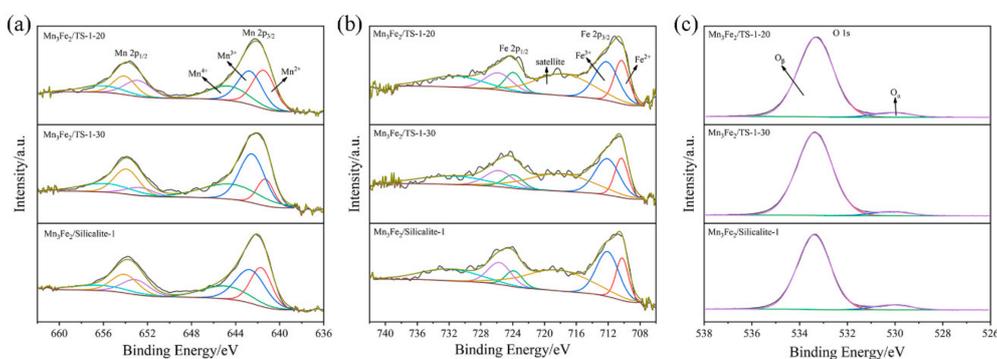


Figure 6. XPS spectra of catalysts: (a) Mn 2p; (b) Fe 2p; (c) O 1s.

Table 3. Surface atom concentrations of samples.

| Sample | Atomic Concentration/at% | | | | |
|--|--------------------------|-------|------|------|------|
| | Si | O | Mn | Fe | Ti |
| $\text{Mn}_3\text{Fe}_2/\text{TS-1-20}$ | 37.37 | 61.78 | 0.53 | 0.13 | 0.19 |
| $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ | 37.33 | 61.86 | 0.50 | 0.15 | 0.16 |
| $\text{Mn}_3\text{Fe}_2/\text{Silicalite-1}$ | 37.07 | 62.22 | 0.52 | 0.19 | - |

It is broadly reported that Mn^{4+} species play a major role in low-temperature NH_3 -SCR reactions [37,42]. Hence, the ratios of $\text{Mn}^{4+}/(\text{Mn}^{4+} + \text{Mn}^{3+} + \text{Mn}^{2+})$ over the catalysts are calculated and listed in Table 4, together with the ratios of $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ and $\text{O}_\beta/(\text{O}_\alpha + \text{O}_\beta)$, which are related to the catalytic performance of catalysts [30,43,44]. The $\text{Mn}^{4+}/(\text{Mn}^{4+} + \text{Mn}^{3+} + \text{Mn}^{2+})$ ratio of

$\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ is 34.6%, which is a significant increase compared to that of $\text{Mn}_3\text{Fe}_2/\text{Silicalite-1}$ (25.0%). The increase of the Mn^{4+} ratio can be attributed to the redox reactions between Mn and Ti species such as $\text{Mn}^{3+} + \text{Ti}^{4+} = \text{Mn}^{4+} + \text{Ti}^{3+}$, $\text{Mn}^{2+} + 2\text{Ti}^{4+} = \text{Mn}^{4+} + 2\text{Ti}^{3+}$ [40]. However, the ratio of Mn^{4+} remains unchanged in $\text{Mn}_3\text{Fe}_2/\text{TS-1-20}$, which can be attributed to the formation of anatase on the supporter. As mentioned above, the excessive Ti species generate anatase on the surface of the supporter, which is reported to inhibit the electron transfer between Mn species and the supporter [42]. The $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ ratio displays a slight decrease when the Ti species are introduced into the supporter, which can be attributed to redox equilibrium between Fe and Ti species like $\text{Fe}^{3+} + \text{Ti}^{3+} = \text{Fe}^{2+} + \text{Ti}^{4+}$ [45]. According to the previously reported literature, surface adsorbed oxygen species (O_β) show more reactive than lattice oxygen (O_α) in the low-temperature NH_3 -SCR reaction, due to their outstanding mobility [46,47]. As shown in Table 4, the incorporation of Ti species increases the $\text{O}_\beta/(\text{O}_\alpha + \text{O}_\beta)$ ratio, while the excessive Ti species consume the surface oxygen mainly because of the formation of anatase. In summary, $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ tends to show the optimal catalytic performance, due to its highest ratio of Mn^{4+} and surface adsorbed oxygen species.

Table 4. The chemical states and relative concentration ratios for different elements.

| Samples | Atomic Ratio/% | | |
|--|---|--|---|
| | $\text{Mn}^{4+}/(\text{Mn}^{4+} + \text{Mn}^{3+} + \text{Mn}^{2+})$ | $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ | $\text{O}_\beta/(\text{O}_\alpha + \text{O}_\beta)$ |
| $\text{Mn}_3\text{Fe}_2/\text{TS-1-20}$ | 25.6 | 59.1 | 94.37 |
| $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ | 34.6 | 62.9 | 95.01 |
| $\text{Mn}_3\text{Fe}_2/\text{Silicalite-1}$ | 25.0 | 65.5 | 93.01 |

2.3. Redox Properties of Samples

The redox properties of the catalysts are closely related to the catalytic performance in the NH_3 -SCR reaction. Therefore, H_2 temperature-programmed reduction (H_2 -TPR) is performed to characterize the redox properties of the catalysts and the results are exhibited in Figure 7 and Table 5. All the catalysts display three reduction peaks between 400 and 700 °C. The reduction peaks centered at 430 °C can be correlated with the simultaneous reduction of MnO_2 and Fe_2O_3 (i.e., $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$, $\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$ and $\text{Fe}_2\text{O}_3 \rightarrow \text{FeO}$) [25,48]. The peaks centered at 580 °C can be assigned to the reduction of Mn_3O_4 , while the peaks above 660 °C can be relevant to the reduction of FeO [48]. As shown in Table 5, when Ti species are introduced into the catalysts, the total area of the reduction peaks reaches 776 a.u., which has an increase of 20% compared to that in $\text{Mn}_3\text{Fe}_2/\text{Silicalite-1}$. Since the area of the reduction peak corresponds to the H_2 consumption, the redox properties of the catalysts are significantly enhanced after the incorporation of Ti species, which is beneficial to promote the NH_3 -SCR reaction at low temperatures.

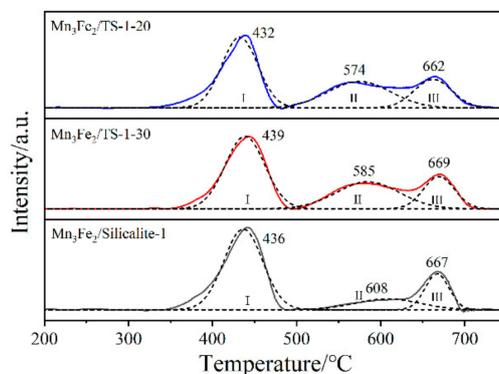


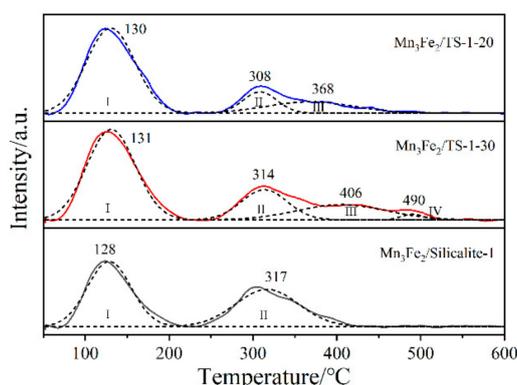
Figure 7. H_2 temperature-programmed reduction (H_2 -TPR) profiles of catalysts.

Table 5. The peak temperature and H₂ consumption of samples from H₂-TPR.

| Samples | Peak Temperature/°C | | | H ₂ Consumption/a.u. | | | |
|---|---------------------|-----------------|------------------|---------------------------------|-----------------|------------------|--------------------|
| | T _I | T _{II} | T _{III} | S _I | S _{II} | S _{III} | S _{total} |
| Mn ₃ Fe ₂ /TS-1-20 | 432 | 574 | 662 | 356 | 231 | 150 | 737 |
| Mn ₃ Fe ₂ /TS-1-30 | 439 | 585 | 669 | 400 | 236 | 140 | 776 |
| Mn ₃ Fe ₂ /Silicalite-1 | 436 | 608 | 667 | 436 | 96 | 119 | 651 |

2.4. Surface Acidity of Samples

The surface acidity is another important factor in low-temperature SCR reaction. Hence, NH₃ temperature-programmed desorption (NH₃-TPD) is used to analyze the surface acidity of the catalysts, and the results are exhibited in Figure 8. For Mn₃Fe₂/Silicalite-1, it displays two desorption peaks labeled as I and II, which correspond to weak (<200 °C) and medium-strong (200~400 °C) acid sites, respectively [43,49]. However, more desorption peaks can be observed in Mn₃Fe₂/TS-1-30 and Mn₃Fe₂/TS-1-20, which are related to medium-strong acid sites [43,49], indicating that the new Lewis acid sites are related with the incorporation of Ti species and thus benefit the adsorption of NH₃. The total acid amounts of these catalysts are calculated from TPD results and listed in Table 6. It shows that the acid amounts of Mn₃Fe₂/TS-1-30 and Mn₃Fe₂/TS-1-20 are larger than that of Mn₃Fe₂/Silicalite-1. Mn₃Fe₂/TS-1-30, especially, exhibits a remarkable increase (about 50%) in the acid amount, compared to that of Mn₃Fe₂/Silicalite-1. In summary, Ti species improve the surface acidity of the catalysts, which is beneficial for the adsorption of NH₃, and finally enhances the catalytic performance in the low-temperature SCR reaction.

**Figure 8.** NH₃ temperature-programmed desorption (NH₃-TPD) profiles of catalysts.**Table 6.** The peak temperature and acid amount of samples from NH₃-TPD.

| Samples | Peak Temperature/°C | | | | Acid Amount/a.u. | | | | |
|---|---------------------|-----------------|------------------|-----------------|------------------|-----------------|------------------|-----------------|--------------------|
| | T _I | T _{II} | T _{III} | T _{IV} | S _I | S _{II} | S _{III} | S _{IV} | S _{total} |
| Mn ₃ Fe ₂ /TS-1-20 | 130 | 308 | 368 | - | 373 | 65 | 88 | - | 526 |
| Mn ₃ Fe ₂ /TS-1-30 | 131 | 314 | 406 | 490 | 399 | 126 | 123 | 11 | 659 |
| Mn ₃ Fe ₂ /Silicalite-1 | 128 | 317 | - | - | 259 | 213 | - | - | 472 |

Figure 9 displays the in situ diffuse reflectance infrared Fourier transform (in situ DRIFTS) of NH₃ adsorption in a temperature range between 60 and 330 °C, to further distinguish the Brønsted acid sites (labeled as B acid) and Lewis acid sites (labeled as L acid) on the surface of the catalysts. It is widely reported that the bands at 1602–1605 cm⁻¹, 1225–1227 cm⁻¹, 1142–1163 cm⁻¹ and 1059–1064 cm⁻¹ can be attributed to asymmetric and symmetric bending vibrations of the coordinated NH₃ linked to L acid sites [50,51]. The bands at 1428–1448 cm⁻¹ and 1737–1748 cm⁻¹ can be assigned to the NH₄⁺ species on B acid sites [52]. The bands at 1550–1554 cm⁻¹ and 1302–1324 cm⁻¹ can be attributed to NH₂ species,

which are transformed from the coordinated NH_3 [53,54]. Moreover, with the increase of temperature, the bands linked to B acid sites are found to decrease more noticeable than these linked to L acid sites, indicating that the bands assigned to L acid sites are more stable at a higher temperature [37]. Besides, by comparing the spectra of $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ (20) with that of $\text{Mn}_3\text{Fe}_2/\text{Silicalite-1}$, the intensity of bands at $1602\text{--}1605\text{ cm}^{-1}$ and $1428\text{--}1448\text{ cm}^{-1}$ is enhanced after the incorporation of Ti species, which indicates that $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ (20) can provide more adsorbed NH_3 for SCR reaction than $\text{Mn}_3\text{Fe}_2/\text{Silicalite-1}$, which can benefit the catalytic activities.

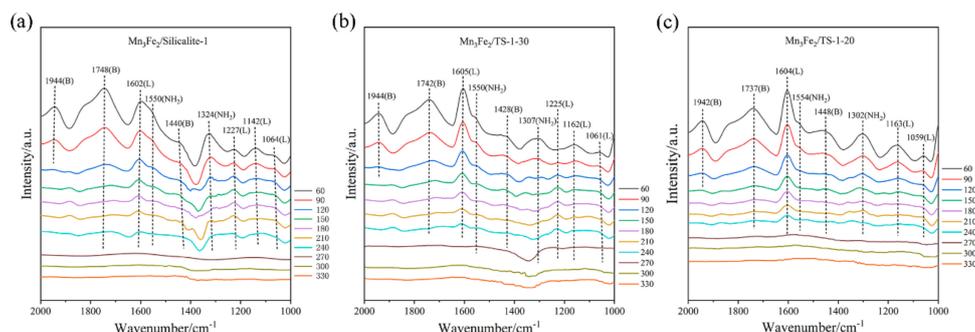


Figure 9. In situ diffuse reflectance infrared Fourier transform (in situ DRIFTS) of NH_3 adsorption of depending on reaction temperatures from 60 to 330 °C: (a) $\text{Mn}_3\text{Fe}_2/\text{Silicalite-1}$; (b) $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$; (c) $\text{Mn}_3\text{Fe}_2/\text{TS-1-20}$.

2.5. Catalytic Performance of Samples

Figure 10a shows the catalytic activities of the catalysts under different reaction temperatures. It can be seen from the figure that $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ exhibits a NO_x conversion efficiency of 90% at 120 °C, which has an increase of almost 30% compared to that of $\text{Mn}_3\text{Fe}_2/\text{Silicalite-1}$ at the same temperature. In addition, both $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ and $\text{Mn}_3\text{Fe}_2/\text{TS-1-20}$ show an obvious improvement in catalytic activities at low temperatures, especially below 150 °C. The optimized catalysts, $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ can maintain steady NO_x conversion efficiencies above 80% in the temperature range between 110 and 230 °C, with a space velocity of $18,000\text{ h}^{-1}$. Based on the characterization of the catalysts' physical and chemical properties mentioned above, the improvement of low-temperature denitration activity is mainly attributed to the incorporation of Ti species, which enhances the redox properties of the catalysts and provides more surface acid sites for the adsorption of NH_3 .

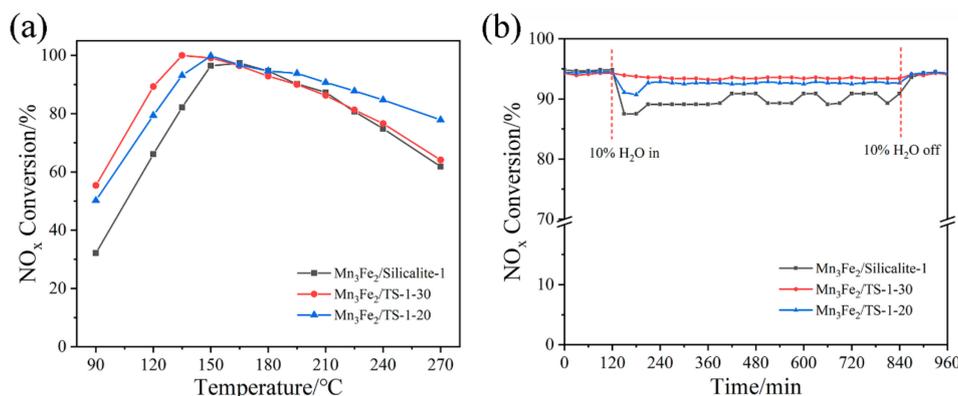


Figure 10. The NH_3 -selective catalytic reduction (SCR) activity of catalysts at the variation of temperature (a); H_2O resistance performance of catalysts at 180 °C (b).

Since zeolites are reported to be sensitive to water vapor [26,28], the H_2O resistance of the catalysts is further studied at the temperature of 180 °C. As shown in Figure 10b, when 10 vol.% H_2O is introduced into the reaction, $\text{Mn}_3\text{Fe}_2/\text{Silicalite-1}$ displays a decrease of about 5% in NO_x conversion

efficiency, while $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ remains unaffected by water vapor. It is widely accepted that the water deactivation is mainly because of the competitive adsorption between NH_3 and water vapor [16,55], and the presence of Ti species further strengthens the hydrophobicity of the catalyst [29,56], thereby improving the H_2O resistance of the catalysts.

3. Materials and Methods

3.1. Preparation of Samples

Silicalite-1 and TS-1 were synthesized by a hydrothermal template method, according to the previous literature [57,58]. The tetrapropylammonium hydroxide (TPAOH, 25 wt.% aqueous solution, Beijing Innochem Technology Co., Ltd., China) was served as a microporous template, while ethyl silicate (TEOS, Tianjin Guangfu Fine Chemical Research Institute, China) and tetrabutyl titanate (TBOT, Beijing Tongguang Fine Chemical Company, China) were served as the source of silicon and titanium, respectively. The molar composition of the synthesis solution was: $\text{SiO}_2:\text{TiO}_2:\text{TPAOH}:\text{H}_2\text{O} = 1:(0\sim 0.05):0.2:7$. Firstly, TEOS was added dropwise into 12.8 g aqueous solution of TPAOH at 40 °C with constant magnetic stirring while TBOT was dissolved in 10 g isopropanol. Secondly, the hydrolysis solutions of TEOS and TBOT were mixed and then heated up to 80 °C to distill off isopropanol. Then, the mixture was transferred into a stainless steel autoclave and then kept in an oven at 160 °C for 48 h. Afterwards, the white precipitation was washed by deionized water and ethanol for three times, respectively. Finally, the products were dried at 80 °C overnight, followed by calcination at 550 °C in the air for 6 h. The prepared samples without titanium labeled as Silicalite-1, while others with feeding $n(\text{Si}/\text{Ti})$ of 30, 20 were labeled as TS-1-30 and TS-1-20, respectively.

$\text{MnO}_x\text{-FeO}_x$ catalysts were synthesized through the wet impregnation method. Manganese nitrate ($\text{Mn}(\text{NO}_3)_2$, 50 wt.% aqueous solution, Saen Chemical Technology (Shanghai) Co., Ltd., China) and iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, 99.9%, Beijing Tongguang Fine Chemical Company, China) were dissolved in deionized water as precursors and zeolites including Silicalite-1 and TS-1 were immersed into solution as supporters. The mass ratio of the mixture was: $\text{Mn}:\text{Fe}:\text{supporter}$ (Silicalite-1 or TS-1) = 3:2:100, which is favorable for $\text{NH}_3\text{-SCR}$ reaction according to the previous-reported researches [25,30]. After magnetic stirring at room temperature for 2 h, the mixture was transferred into an oven at 110 °C overnight, and followed by calcination at 500 °C in the air for 4 h. The samples were labeled as $\text{Mn}_3\text{Fe}_2/\text{Silicalite-1}$, $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ and $\text{Mn}_3\text{Fe}_2/\text{TS-1-20}$, respectively.

3.2. Characterization

X-ray diffraction (XRD) patterns of as-prepared samples were collected by a powder X-ray diffractometer (Rigaku Dmax-2400, RIGAKU, Tokyo, Japan) with $\text{Cu-K}\alpha$ target. Fourier transform infrared (FT-IR) spectra were collected on a FT-IR spectrophotometer (Nicolet iS50, ThermoFisher, Waltham, MA, USA). The textural properties of as-prepared samples were investigated using a nitrogen adsorption apparatus (ASAP2020, Micromeritics, Norcross, GA, USA) at 77 K. Specific surface area, pore volume and pore size were calculated by Brunauer-Emmett-Teller (BET), single point and Barrett-Joyner-Halenda (BJH) methods, respectively. Surface morphologies of as-prepared samples were carried out on a field emission scanning electron microscope (Merlin Compact, ZEISS, Oberkochen, Germany) operating at 10 kV. Transmission electron microscopy (TEM) images of as-prepared samples were screened on a transmission electron microscope (JEM-2100F, JEOL, Tokyo, Japan) operating at 200 kV. The chemical composition of as-prepared samples was measured by an inductively coupled plasma-atomic emission spectrometer (Thermo iCAP6000 ICP-OES, ThermoFisher, Waltham, MA, USA). The surface chemical species of as-prepared samples were characterized by an X-ray photoelectron spectroscopy (AXIS Supra, Kratos Analytical Ltd., Manchester, UK) with $\text{Al K}\alpha$ radiation. H_2 temperature-programmed reduction ($\text{H}_2\text{-TPR}$) and NH_3 temperature-programmed desorption ($\text{NH}_3\text{-TPD}$) experiments were carried out on a chemisorption analyzer (ChemBET Pulsar TPR/TPD, Quantachrome, Boynton Beach, FL, USA). In situ diffuse reflectance infrared Fourier

transform (in situ DRIFTS) of NH_3 adsorption were obtained from a FT-IR spectrophotometer (Nicolet 6700, Thermo Fisher, USA), by accumulating 32 scans with a resolution of 4 cm^{-1} . The samples were firstly pretreated under a high purified N_2 stream at $400 \text{ }^\circ\text{C}$ for 1 h to remove physisorbed water and other impurities. Then the background spectra were obtained at target temperatures during the cooling procedure. Subsequently, the samples were exposed to a stream of NH_3/N_2 (1 vol.% NH_3) at room temperature, followed by purging with N_2 for 30 min. The desorption of NH_3 studies were measured by heating pre-adsorbed samples, and the spectra were recorded at stepped target temperatures by eliminating the corresponding background reference.

3.3. NH_3 -SCR Activity Measurements

The NH_3 -SCR catalytic performances were tested in a fixed-bed quartz reactor (6 mm of internal diameter) in the temperature range from 90 to $270 \text{ }^\circ\text{C}$, with a GHSV of $18,000 \text{ h}^{-1}$. The reaction gas mixture was consisted of 500 ppm NO, 500 ppm NH_3 , 3 vol.% O_2 , 10 vol.% H_2O (if applied) and N_2 in balance. Firstly, 200 mg catalyst was pretreated with N_2 at $200 \text{ }^\circ\text{C}$ for 30 min to eliminate physisorbed water. The concentrations of NO and NO_2 were obtained through a flue gas analyzer (Testo 350 Pro, Testo, Black forest, Germany) when the catalytic reaction substantially reached a steady state at every target temperature. Moreover, H_2O resistance of the catalysts for low-temperature NH_3 -SCR reaction was evaluated at the target temperature. NO_x conversion efficiency was calculated according to the following formula:

$$\text{NO}_x \text{ conversion efficiency}(\%) = \left(1 - \frac{[\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}}\right) \times 100\% \quad (1)$$

$$[\text{NO}_x] = [\text{NO}] + [\text{NO}_2] \quad (2)$$

where $[\text{NO}_x]_{\text{in}}$ and $[\text{NO}_x]_{\text{out}}$ refer to inlet and outlet concentrations of NO_x at steady state, respectively.

4. Conclusions

In this work, silicalite-1 and TS-1 were applied as supporters to load MnO_x and FeO_x nanoparticles as active components for the low-temperature NH_3 -SCR reaction. $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ maintains NO_x conversion efficiencies above 80% when the range of temperature is from 110 to $230 \text{ }^\circ\text{C}$. Moreover, $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ can maintain a denitration efficiency of 94% in the presence of 10 vol.% H_2O at $180 \text{ }^\circ\text{C}$ for over 12 h. Its excellent catalytic performance and H_2O resistance can be attributed to having much more surface acid sites and the stronger redox ability of its active components, which can be explained by the incorporation of Ti species. Therefore, the superior denitration ability and H_2O resistance of $\text{Mn}_3\text{Fe}_2/\text{TS-1-30}$ will make it a practical catalyst for industrial largescale denitration at low temperatures.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/5/566/s1>, Figure S1: STEM images and EDS mappings of the supporters: (a) TS-1-30; (b) TS-1-20.

Author Contributions: Conceptualization, J.G. and X.W.; formal analysis, J.G., R.D. and Y.C.; writing—original draft preparation, J.G.; writing—review and editing, J.G., R.D., W.C. and X.W.; supervision, X.W.; project administration, L.L.; funding acquisition, L.L. and X.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Grant No. 51672006 and 51472006), the Ministry of Land and Resources Public Welfare Industry Research Project (No. 201511062-02) and the National key research and development plan (No. 2018YFC1901505).

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

References

1. Busca, G.; Lietti, L.; Ramis, G.; Berti, F. Chemical and mechanistic aspects of the selective catalytic reduction of NO_x by ammonia over oxide catalysts: A review. *Appl. Catal. B Environ.* **1998**, *18*, 1–36. [[CrossRef](#)]
2. Wang, X.; Liu, Y.; Wu, Z. Highly active NbOPO₄ supported Cu-Ce catalyst for NH₃-SCR reaction with superior sulfur resistance. *Chem. Eng. J.* **2020**, *382*, 122941. [[CrossRef](#)]
3. Paolucci, C.; Khurana, I.; Parekh, A.A.; Li, S.; Shih, A.J.; Li, H.; Di Iorio, J.R.; Albarracin-Caballero, J.D.; Yezerets, A.; Miller, J.T.; et al. Dynamic multinuclear sites formed by mobilized copper ions in NO_x selective catalytic reduction. *Science* **2017**, *357*, 898–903. [[CrossRef](#)]
4. Gillot, S.; Tricot, G.; Vezin, H.; Dacquin, J.-P.; Dujardin, C.; Granger, P. Development of stable and efficient CeVO₄ systems for the selective reduction of NO_x by ammonia: Structure-activity relationship. *Appl. Catal. B Environ.* **2017**, *218*, 338–348. [[CrossRef](#)]
5. Mou, X.; Zhang, B.; Li, Y.; Yao, L.; Wei, X.; Su, D.S.; Shen, W. Rod-Shaped Fe₂O₃ as an Efficient Catalyst for the Selective Reduction of Nitrogen Oxide by Ammonia. *Angew. Chem. Int. Ed.* **2012**, *51*, 2989. [[CrossRef](#)]
6. Chen, L.; Si, Z.; Wu, X.; Weng, D. DRIFT study of CuO-CeO₂-TiO₂ mixed oxides for NO_x reduction with NH₃ at low temperatures. *ACS Appl. Mater. Interfaces* **2014**, *6*, 8134–8145. [[CrossRef](#)]
7. Gao, F.; Tang, X.; Yi, H.; Li, J.; Zhao, S.; Wang, J.; Chu, C.; Li, C. Promotional mechanisms of activity and SO₂ tolerance of Co- or Ni-doped MnO_x-CeO₂ catalysts for SCR of NO_x with NH₃ at low temperature. *Chem. Eng. J.* **2017**, *317*, 20–31. [[CrossRef](#)]
8. Fang, C.; Zhang, D.; Cai, S.; Zhang, L.; Huang, L.; Li, H.; Maitarad, P.; Shi, L.; Gao, R.; Zhang, J. Low-temperature selective catalytic reduction of NO with NH₃ over nanoflaky MnO_x on carbon nanotubes in situ prepared via a chemical bath deposition route. *Nanoscale* **2013**, *5*, 9199. [[CrossRef](#)] [[PubMed](#)]
9. Chen, Y.; Zhang, Z.; Liu, L.; Mi, L.; Wang, X. In situ DRIFTS studies on MnO_x nanowires supported by activated semi-coke for low temperature selective catalytic reduction of NO_x with NH₃. *Appl. Surf. Sci.* **2016**, *366*, 139–147. [[CrossRef](#)]
10. Zhang, C.; Chen, T.; Liu, H.; Chen, D.; Xu, B.; Qing, C. Low temperature SCR reaction over Nano-Structured Fe-Mn Oxides: Characterization, performance, and kinetic study. *Appl. Surf. Sci.* **2018**, *457*, 1116–1125. [[CrossRef](#)]
11. Yang, J.; Ren, S.; Zhang, T.; Su, Z.; Long, H.; Kong, M.; Yao, L. Iron doped effects on active sites formation over activated carbon supported Mn-Ce oxide catalysts for low-temperature SCR of NO. *Chem. Eng. J.* **2020**, *379*, 122398. [[CrossRef](#)]
12. Pan, W.-G.; Hong, J.-N.; Guo, R.-T.; Zhen, W.-L.; Ding, H.-L.; Jin, Q.; Ding, C.-G.; Guo, S.-Y. Effect of support on the performance of Mn-Cu oxides for low temperature selective catalytic reduction of NO with NH₃. *J. Ind. Eng. Chem.* **2014**, *20*, 2224–2227. [[CrossRef](#)]
13. Chen, Z.; Wang, F.; Li, H.; Yang, Q.; Wang, L.; Li, X. Low-Temperature Selective Catalytic Reduction of NO_x with NH₃ over Fe-Mn Mixed-Oxide Catalysts Containing Fe₃Mn₃O₈ Phase. *Ind. Eng. Chem. Res.* **2011**, *51*, 202–212. [[CrossRef](#)]
14. Liu, Z.; Yi, Y.; Zhang, S.; Zhu, T.; Zhu, J.; Wang, J. Selective catalytic reduction of NO_x with NH₃ over Mn-Ce mixed oxide catalyst at low temperatures. *Catal. Today* **2013**, *216*, 76–81. [[CrossRef](#)]
15. Li, J.H.; Chang, H.Z.; Ma, L.; Hao, J.M.; Yang, R.T. Low-temperature selective catalytic reduction of NO_x with NH₃ over metal oxide and zeolite catalysts-A review. *Catal. Today* **2011**, *175*, 147–156. [[CrossRef](#)]
16. Liu, C.; Shi, J.-W.; Gao, C.; Niu, C. Manganese oxide-based catalysts for low-temperature selective catalytic reduction of NO_x with NH₃: A review. *Appl. Catal. A Gen.* **2016**, *522*, 54–69. [[CrossRef](#)]
17. Wu, S.; Zhang, L.; Wang, X.; Zou, W.; Cao, Y.; Sun, J.; Tang, C.; Gao, F.; Deng, Y.; Dong, L. Synthesis, characterization and catalytic performance of FeMnTiO_x mixed oxides catalyst prepared by a CTAB-assisted process for mid-low temperature NH₃-SCR. *Appl. Catal. A Gen.* **2015**, *505*, 235–242. [[CrossRef](#)]
18. Cao, F.; Su, S.; Xiang, J.; Wang, P.; Hu, S.; Sun, L.; Zhang, A. The activity and mechanism study of Fe-Mn-Ce/γ-Al₂O₃ catalyst for low temperature selective catalytic reduction of NO with NH₃. *Fuel* **2015**, *139*, 232–239. [[CrossRef](#)]
19. Chen, Y.; Wang, J.; Yan, Z.; Liu, L.; Zhang, Z.; Wang, X. Promoting effect of Nd on the reduction of NO with NH₃ over CeO₂ supported by activated semi-coke: An in situ DRIFTS study. *Catal. Sci. Technol.* **2015**, *5*, 2251–2259. [[CrossRef](#)]

20. Wang, J.; Yan, Z.; Liu, L.; Chen, Y.; Zhang, Z.; Wang, X. In situ DRIFTS investigation on the SCR of NO with NH₃ over V₂O₅ catalyst supported by activated semi-coke. *Appl. Surf. Sci.* **2014**, *313*, 660–669. [[CrossRef](#)]
21. Su, Y.; Fan, B.; Wang, L.; Liu, Y.; Huang, B.; Fu, M.; Chen, L.; Ye, D. MnO_x supported on carbon nanotubes by different methods for the SCR of NO with NH₃. *Catal. Today* **2013**, *201*, 115–121. [[CrossRef](#)]
22. Lou, X.; Liu, P.; Li, J.; Li, Z.; He, K. Effects of calcination temperature on Mn species and catalytic activities of Mn/ZSM-5 catalyst for selective catalytic reduction of NO with ammonia. *Appl. Surf. Sci.* **2014**, *307*, 382–387. [[CrossRef](#)]
23. Seo, C.-K.; Choi, B.; Kim, H.; Lee, C.-H.; Lee, C.-B. Effect of ZrO₂ addition on de-NO_x performance of Cu-ZSM-5 for SCR catalyst. *Chem. Eng. J.* **2012**, *191*, 331–340. [[CrossRef](#)]
24. Lv, G.; Bin, F.; Song, C.; Wang, K.; Song, J. Promoting effect of zirconium doping on Mn/ZSM-5 for the selective catalytic reduction of NO with NH₃. *Fuel* **2013**, *107*, 217–224. [[CrossRef](#)]
25. Wang, T.; Wan, Z.; Yang, X.; Zhang, X.; Niu, X.; Sun, B. Promotional effect of iron modification on the catalytic properties of Mn-Fe/ZSM-5 catalysts in the Fast SCR reaction. *Fuel Process. Technol.* **2018**, *169*, 112–121. [[CrossRef](#)]
26. Du, T.; Qu, H.; Liu, Q.; Zhong, Q.; Ma, W. Synthesis, activity and hydrophobicity of Fe-ZSM-5@silicalite-1 for NH₃-SCR. *Chem. Eng. J.* **2015**, *262*, 1199–1207. [[CrossRef](#)]
27. Vu, D.V.; Miyamoto, M.; Nishiyama, N.; Ichikawa, S.; Egashira, Y.; Ueyama, K. Catalytic activities and structures of silicalite-1/H-ZSM-5 zeolite composites. *Microporous Mesoporous Mater.* **2008**, *115*, 106–112. [[CrossRef](#)]
28. Serrano, D.P.; Calleja, G.; Botas, J.A.; Gutierrez, F.J. Characterization of adsorptive and hydrophobic properties of silicalite-1, ZSM-5, TS-1 and Beta zeolites by TPD techniques. *Sep. Purif. Technol.* **2007**, *54*, 1–9. [[CrossRef](#)]
29. Li, G.; Wang, X.; Guo, X.; Liu, S.; Zhao, Q.; Bao, X.; Lin, L. Titanium species in titanium silicalite TS-1 prepared by hydrothermal method. *Mater. Chem. Phys.* **2001**, *71*, 195–201. [[CrossRef](#)]
30. Mu, W.; Zhu, J.; Zhang, S.; Guo, Y.; Su, L.; Li, X.; Li, Z. Novel proposition on mechanism aspects over Fe-Mn/ZSM-5 catalyst for NH₃-SCR of NO_x at low temperature: Rate and direction of multifunctional electron-transfer-bridge and in situ DRIFTS analysis. *Catal. Sci. Technol.* **2016**, *6*, 7532–7548. [[CrossRef](#)]
31. Xia, Y.; Zhan, W.; Guo, Y.; Guo, Y.; Lu, G. Fe-Beta zeolite for selective catalytic reduction of NO_x with NH₃: Influence of Fe content. *Chin. J. Catal.* **2016**, *37*, 2069–2078. [[CrossRef](#)]
32. Xu, W.; Zhang, G.; Chen, H.; Zhang, G.; Han, Y.; Chang, Y.; Gong, P. Mn/beta and Mn/ZSM-5 for the low-temperature selective catalytic reduction of NO with ammonia: Effect of manganese precursors. *Chin. J. Catal.* **2018**, *39*, 118–127. [[CrossRef](#)]
33. Cheng, K.; Liu, J.; Zhao, Z.; Wei, Y.; Jiang, G.; Duan, A. Direct synthesis of V-W-Ti nanoparticle catalysts for selective catalytic reduction of NO with NH₃. *RSC Adv.* **2015**, *5*, 45172–45183. [[CrossRef](#)]
34. Hu, H.; Cai, S.; Li, H.; Huang, L.; Shi, L.; Zhang, D. In Situ DRIFTS Investigation of the Low-Temperature Reaction Mechanism over Mn-Doped Co₃O₄ for the Selective Catalytic Reduction of NO_x with NH₃. *J. Phys. Chem. C* **2015**, *119*, 22924–22933. [[CrossRef](#)]
35. Liu, F.; He, H.; Ding, Y.; Zhang, C. Effect of manganese substitution on the structure and activity of iron titanate catalyst for the selective catalytic reduction of NO with NH₃. *Appl. Catal. B Environ.* **2009**, *93*, 194–204. [[CrossRef](#)]
36. Reddy, A.; Gopinath, C.; Chilukuri, S. Selective ortho-methylation of phenol with methanol over copper manganese mixed-oxide spinel catalysts. *J. Catal.* **2006**, *243*, 278–291. [[CrossRef](#)]
37. Xiong, Y.; Tang, C.; Yao, X.; Zhang, L.; Li, L.; Wang, X.; Deng, Y.; Gao, B.; Dong, L. Effect of metal ions doping (M=Ti⁴⁺, Sn⁴⁺) on the catalytic performance of MnO_x/CeO₂ catalyst for low temperature selective catalytic reduction of NO with NH₃. *Appl. Catal. A Gen.* **2015**, *495*, 206–216. [[CrossRef](#)]
38. Zhu, L.; Zhang, L.; Qu, H.; Zhong, Q. A study on chemisorbed oxygen and reaction process of Fe-CuO_x/ZSM-5 via ultrasonic impregnation method for low-temperature NH₃-SCR. *J. Mol. Catal. A Chem.* **2015**, *409*, 207–215. [[CrossRef](#)]
39. Tan, P. Active phase, catalytic activity, and induction period of Fe/zeolite material in nonoxidative aromatization of methane. *J. Catal.* **2016**, *338*, 21–29. [[CrossRef](#)]
40. Li, L.; Wu, Y.; Hou, X.; Chu, B.; Nan, B.; Qin, Q.; Fan, M.; Sun, C.; Li, B.; Dong, L.; et al. Investigation of Two-Phase Intergrowth and Coexistence in Mn-Ce-Ti-O Catalysts for the Selective Catalytic Reduction of NO with NH₃: Structure-Activity Relationship and Reaction Mechanism. *Ind. Eng. Chem. Res.* **2018**, *58*, 849–862. [[CrossRef](#)]

41. Meng, D.; Zhan, W.; Guo, Y.; Guo, Y.; Wang, L.; Lu, G. A Highly Effective Catalyst of Sm-MnO_x for the NH₃-SCR of NO_x at Low Temperature: Promotional Role of Sm and Its Catalytic Performance. *ACS Catal.* **2015**, *5*, 5973–5983. [[CrossRef](#)]
42. Yao, X.; Chen, L.; Cao, J.; Chen, Y.; Tian, M.; Yang, F.; Sun, J.; Tang, C.; Dong, L. Enhancing the deNO performance of MnO_x/CeO₂-ZrO₂ nanorod catalyst for low-temperature NH₃-SCR by TiO₂ modification. *Chem. Eng. J.* **2019**, *369*, 46–56. [[CrossRef](#)]
43. You, X.; Sheng, Z.; Yu, D.; Yang, L.; Xiao, X.; Wang, S. Influence of Mn/Ce ratio on the physicochemical properties and catalytic performance of graphene supported MnO_x-CeO₂ oxides for NH₃-SCR at low temperature. *Appl. Surf. Sci.* **2017**, *423*, 845–854. [[CrossRef](#)]
44. Zha, K.; Cai, S.; Hu, H.; Li, H.; Yan, T.; Shi, L.; Zhang, D. In Situ DRIFTS Investigation of Promotional Effects of Tungsten on MnO_x-CeO₂/meso-TiO₂ Catalysts for NO_x Reduction. *J. Phys. Chem. C* **2017**, *121*, 25243–25254. [[CrossRef](#)]
45. Kang, M.; Park, E.D.; Kim, J.M.; Yie, J.E. Cu–Mn mixed oxides for low temperature NO reduction with NH₃. *Catal. Today* **2006**, *111*, 236–241. [[CrossRef](#)]
46. Chen, J.; Chen, X.; Chen, X.; Xu, W.; Xu, Z.; Jia, H.; Chen, J. Homogeneous introduction of CeO_y into MnO_x-based catalyst for oxidation of aromatic VOCs. *Appl. Catal. B Environ.* **2018**, *224*, 825–835. [[CrossRef](#)]
47. Du, J.; Qu, Z.; Dong, C.; Song, L.; Qin, Y.; Huang, N. Low-temperature abatement of toluene over Mn–Ce oxides catalysts synthesized by a modified hydrothermal approach. *Appl. Surf. Sci.* **2018**, *433*, 1025–1035. [[CrossRef](#)]
48. Lin, L.-Y.; Lee, C.-Y.; Zhang, Y.-R.; Bai, H. Aerosol-assisted deposition of Mn-Fe oxide catalyst on TiO₂ for superior selective catalytic reduction of NO with NH₃ at low temperatures. *Catal. Commun.* **2018**, *111*, 36–41. [[CrossRef](#)]
49. Peng, Y.; Wang, D.; Li, B.; Wang, C.; Li, J.; Crittenden, J.; Hao, J. Impacts of Pb and SO₂ Poisoning on CeO₂-WO₃/TiO₂-SiO₂ SCR Catalyst. *Environ. Sci. Technol.* **2017**, *51*, 11943–11949. [[CrossRef](#)]
50. Liu, Y.; Gu, T.; Weng, X.; Wang, Y.; Wu, Z.; Wang, H. DRIFT Studies on the Selectivity Promotion Mechanism of Ca-Modified Ce-Mn/TiO₂ Catalysts for Low-Temperature NO Reduction with NH₃. *J. Phys. Chem. C* **2012**, *116*, 16582–16592. [[CrossRef](#)]
51. Ramis, G.; Yi, L.; Busca, G. Ammonia activation over catalysts for the selective catalytic reduction of NO_x and the selective catalytic oxidation of NH₃. An FT-IR study. *Catal. Today* **1996**, *28*, 373–380. [[CrossRef](#)]
52. Lin, S.D.; Gluhoi, A.C.; Nieuwenhuys, B.E. Ammonia oxidation over Au/MO/γ-Al₂O₃—activity, selectivity and FTIR measurements. *Catal. Today* **2004**, *90*, 3–14. [[CrossRef](#)]
53. Ettireddy, P.R.; Ettireddy, N.; Boningari, T.; Pardemann, R.; Smirniotis, P.G. Investigation of the selective catalytic reduction of nitric oxide with ammonia over Mn/TiO₂ catalysts through transient isotopic labeling and in situ FT-IR studies. *J. Catal.* **2012**, *292*, 53–63. [[CrossRef](#)]
54. Liu, Z.; Zhu, J.; Li, J.; Ma, L.; Woo, S.I. Novel Mn-Ce-Ti mixed-oxide catalyst for the selective catalytic reduction of NO_x with NH₃. *ACS Appl. Mater. Interfaces* **2014**, *6*, 14500–14508. [[CrossRef](#)] [[PubMed](#)]
55. Zhang, S.; Zhang, B.; Liu, B.; Sun, S. A review of Mn-containing oxide catalysts for low temperature selective catalytic reduction of NO_x with NH₃: Reaction mechanism and catalyst deactivation. *RSC Adv.* **2017**, *7*, 26226–26242. [[CrossRef](#)]
56. Chen, H.; Zhang, R.; Bao, W.; Wang, H.; Wang, Z.; Wei, Y. Effective catalytic abatement of indoor formaldehyde at room temperature over TS-1 supported platinum with relatively low content. *Catal. Today* **2019**. [[CrossRef](#)]
57. Kuperman, A.; Nadimi, S.; Oliver, S.; Ozin, G.A.; Garces, J.M.; Olken, M.M. Non-aqueous Synthesis of Giant Crystal of Zeolites and Molecular Sieves. *Nature* **1993**, *365*, 239–242. [[CrossRef](#)]
58. Zuo, Y.; Liu, M.; Zhang, T.; Hong, L.; Guo, X.; Song, C.; Chen, Y.; Zhu, P.; Jaye, C.; Fischer, D. Role of pentahedrally coordinated titanium in titanium silicalite-1 in propene epoxidation. *RSC Adv.* **2015**, *5*, 17897–17904. [[CrossRef](#)]

