Precursor Effect on Mn-Fe-Ce/TiO₂ Catalysts for Selective Catalytic Reduction of NO with NH₃ at Low Temperatures

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Abstract: Preparation of Mn/TiO₂, Mn-Fe/TiO₂, and Mn-Fe-Ce/TiO₂ by the deposition-precipitation (DP) method can afford very active catalysts for low-temperature NH₃-SCR (selective catalytic reduction of NO with NH₃). The effect of precursor choice (nitrate vs. acetate) of Mn, Fe, and Ce on the physiochemical properties including thermal stability and the resulting SCR activity were investigated. The resulting materials were characterized by N₂-Physisorption, XRD (Powder X-ray diffraction), XPS (X-ray photoelectron spectroscopy), H₂-TPR (temperature-programmed reduction with hydrogen), and the oxidation of NO to NO₂ measured at 300 °C. Among all the prepared catalysts 5Mnₐcₑ/Ti, 25Mnₐcₑ₂₅Fₑ₂₅Nᵢ₄/Ti, and 25Mnₐcₑ₂₅Fₑ₂₅Cₑ₀₅Acₑ/Ti showed superior SCR activity at low temperature. The superior activity of the latter two materials is likely attributable to the presence of amorphous active metal oxide phases (manganese-, iron- and cerium-oxide) and the ease of the reduction of metal oxides on TiO₂. Enhanced ability to convert NO to NO₂, which can promote fast-SCR like pathways, could be another reason. Cerium was found to stabilize amorphous manganese oxide phases when exposed to high temperatures.

Keywords: precursor effect; thermal stability; deposition-precipitation; NH₃-SCR of NO; MnFe/TiO₂

1. Introduction

NH₃-SCR (selective catalytic reduction of NOₓ with NH₃) with V₂O₅-WO₃/TiO₂ as the catalyst is used successfully in stationary plants [1–5]. The support of choice is TiO₂ (anatase form) due to its higher surface area relative to rutile phase and the fact that SO₃ does not deteriorate the TiO₂ support. The commercial catalyst exhibits high selectivity and activity in the NH₃-SCR of NO at 300–400 °C [3–5]. In order to operate at this temperature, the SCR unit is usually installed at a high dust position.

However, by placing the SCR unit at the high dust position, the catalyst’s life is shortened due to the high content of ash with alkali metals in the flue gas [6–8]. Therefore, the tail-end position, which is located behind the SO₂/SO₃-removing unit is attractive. Decreased erosion and fouling at the low dust level also increases the catalyst’s lifetime [9]. In order to avoid costly reheating of the flue gas to around 350 °C, tail-end placement necessitates the SCR catalyst to be significantly more active than the vanadia-tungsta based one.

In recent years, a large number of research articles on NH₃-SCR of NO at low-temperature have been published. Among the reported catalysts, Mn/TiO₂ based formulations are the most promising [10,11]. Furthermore, bimetallic Mn catalysts showed higher activities and selectivities. Hence, Mn-Fe/TiO₂ [12–15], MnOx-CeO₂ [16], and Mn-Ce/TiO₂ [17,18] have been reported to be highly active bimetallic catalysts for NH₃-SCR of
NO at low temperatures. Recently, we reported highly active low temperature Mn-Fe/TiO2 catalysts prepared by deposition-precipitation using ammonia carbamate as a precipitating agent [19].

The low-temperature SCR activity of the MnOx catalysts depends on the precursor, preparation method, and metal loading. Kapteijn et al. [20] reported that a Mn/Al2O3 catalyst was more active when prepared with Mn-acetate than with Mn-nitrate. Likewise, Li et al. [21] concluded that a Mn-acetate derived Mn/TiO2 catalyst had better activity than its Mn-nitrate based version. However, Peña et al. [22] showed that a Mn/TiO2 catalyst prepared from manganese nitrate and calcined at 400 °C had better activity at lower temperatures than a catalyst obtained from manganese acetate. Detailed investigation of the precursor effect on more active formulations like Mn-Fe/TiO2 and Mn-Fe-Ce/TiO2 catalysts has not been reported.

The optimum Mn loading of low temperature Mn/TiO2 catalysts was reported to be 20 wt.% [22] while the optimum loadings of Mn and Fe in Mn-Fe/TiO2 catalysts synthesized by impregnation were both 10 wt.% [14]. In our previous article [19], we reported that it was possible to further reduce the total metal loading on Mn/TiO2 catalysts from 20 wt.% to 5 wt.% with a change in the method of synthesis from conventional impregnation to deposition, while the total metal loading of the Mn-Fe/TiO2 catalysts could be reduced from 35 wt.% to 25 wt.% Catalysts based on Mn-Fe/TiO2 contain high amounts of active metals (about 20–25 wt.%) compared to the traditional V2O5-WO3/TiO2 system (about 7–10 wt.%). Additionally, unsupported manganese oxide in hollandite form [23] and MnOx-CeO2 [16] exhibited high NH3-SCR activity at low temperatures.

The present article deals with the preparation of Mn/TiO2, Mn-Fe/TiO2, and Mn-Fe-Ce/TiO2 using several metal precursors. Various methods of characterization were employed to understand the differences in catalyst properties and activities.

2. Results and Discussion

The SCR NO conversion profiles of the 5MnNit and 5MnAce supported catalysts are shown in Figure 1. Among the catalysts studied, Mn deposited on TiO2 showed superior catalytic activity followed by ZrO2 and Al2O3. In particular, MnAce/Ti was more active compared to the MnNit/Ti. At 250 °C, the MnAce/Ti and MnNit/Ti catalysts displayed a NO conversion of 81 and 65%, respectively. The low temperature activity of the Mn/TiO2 catalysts were compared with silica and alumina by Simirniotis et al. [24] and they concluded that Lewis acid sites, a high surface concentration of MnO2, and good redox properties were important in achieving low temperature SCR activity. For further experiments, TiO2 was chosen as the unique support.

![Figure 1](image-url)

Figure 1. NO conversion profiles of: (a) 5MnNit and; (b) 5MnAce on various supports.

Mn/TiO2 doped with transition metals (e.g., Ni, Cu, and Fe) had high resistance to sintering and more favorable Mn dispersion [12]. It is also reported that Mn/TiO2 catalysts promoted with transition metals showed activity for NO oxidation to NO2 [15].
In our previous publication, we reported the promotional effect of Fe on Mn/TiO₂ catalysts and the optimum formulation was found to be 25 Mn₀.₇₅Fe₀.₂₅/Ti using deposition-precipitation [19]. Figure 2a shows the NO conversion profiles of the 25 wt.% Mn₀.₇₅Fe₀.₂₅/Ti catalysts with Mn and Fe precursor combinations as a function of reaction temperature. All the catalysts, except for the 25Mn₀.₇₅NiFe₀.₂₅Ace/Ti catalyst, showed full conversion above 225 °C. The 25Mn₀.₇₅AceFe₀.₂₅Ni/Ti, 25Mn₀.₇₅NiFe₀.₂₅Ni/Ti, 25Mn₀.₇₅AceFe₀.₂₅Ace/Ti, and 25Mn₀.₇₅NiFe₀.₂₅Ace/Ti catalysts exhibited NO conversion of 69.6, 55.6, 47.0, and 43.1% at 150 °C, respectively, illustrating the importance of precursors on catalyst activity.

![Figure 2a](image1.png)

**Figure 2a.** NO conversion profiles of catalysts prepared by different precursors: (a) 25Mn₀.₇₅Fe₀.₂₅/Ti; (b) 25Mn₀.₇₅Fe₀.₂₅Ce₀.₀₅/Ti.

It is also well known that the presence of Ce can enhance the SCR performance and selectivity to N₂ [17]. It is also known that the presence of Ce further overcomes the SO₂ deactivation and water inhibition effects [18]. Figure 2b shows the effect of Ce precursor on the optimum 25Mn₀.₇₅AceFe₀.₂₅Ni/Ti catalyst. The presence of Ce in the 25Mn₀.₇₅AceFe₀.₂₀NiCe₀.₀₅Ace/Ti catalyst showed slightly better performance while 25Mn₀.₇₅AceFe₀.₂₀NiCe₀.₀₅Ni/Ti showed less performance than the previously optimized 25Mn₀.₇₅AceFe₀.₂₅Ni/Ti catalyst. This further confirms the sensitivity of SCR catalysts to the choice of precursors. The 25Mn₀.₇₅AceFe₀.₂₅Ni/Ti, 25Mn₀.₇₅AceFe₀.₂₀NiCe₀.₀₅Ace/Ti, and 25Mn₀.₇₅AceFe₀.₂₀NiCe₀.₀₅Ni/Ti catalysts displayed NO conversions of 69.6, 73.0, and 54.4% at 150 °C, respectively. Table 1 summarizes the N₂O formation data obtained at 150 °C over the 25Mn₀.₇₅AceFe₀.₂₅Ni/Ti, 25Mn₀.₇₅AceFe₀.₂₀NiCe₀.₀₅Ace/Ti, and 25Mn₀.₇₅AceFe₀.₂₀NiCe₀.₀₅Ni/Ti catalysts, which respectively produced 35, 15, and 20 ppm of N₂O under wet conditions (2.3 vol% H₂O). Thus, the presence of Ce can increase the selectivity to N₂. A moderate Ce content in Mn-Fe/TiO₂ catalysts contributed to decreased N₂O formation by hindering the over oxidation of NH₃, the dominant step in N₂O formation data at 150 °C.

![Figure 2b](image2.png)

**Figure 2b.** NO conversion profiles of catalysts with Mn and Fe precursor combinations as a function of reaction temperature.

**Table 1.** N₂O formation data at 150 °C.

| Catalyst                  | NO Conv. (%) | 2.3 vol.% H₂O | Sel. N₂O (%) | 10 vol.% H₂O | Sel. N₂O (%) |
|---------------------------|--------------|----------------|--------------|--------------|--------------|
| 25Mn₀.₇₅AceFe₀.₂₅Ni/Ti    | 69.6         | 35             | 5.0          | 0            | 0            |
| 25Mn₀.₇₅AceFe₀.₂₀NiCe₀.₀₅Ace/Ti | 73.0     | 15             | 2.1          | 0            | 0            |
| 25Mn₀.₇₅AceFe₀.₂₀NiCe₀.₀₅Ni/Ti | 54.4       | 20             | 3.7          | 0            | 0            |

Figure 3a shows the NO conversion profiles of 20–30 wt.% Mn₀.₇₅AceFe₀.₂₀NiCe₀.₀₅Ace/Ti catalysts vs. the reaction temperature. The NO conversion was in the following order: 25 Mn₀.₇₅AceFe₀.₂₀NiCe₀.₀₅Ace/Ti > 20 Mn₀.₇₅AceFe₀.₂₀NiCe₀.₀₅Ace/Ti > 30 Mn₀.₇₅AceFe₀.₂₀NiCe₀.₀₅Ace/Ti.
between 150–200 °C. Above 200 °C, the catalysts showed almost 100% NO conversion and it was not possible to discriminate between them. The 20, 25, and 30 wt.% $\text{Mn}_{0.75}\text{Ace}_{0.20}\text{Ni}_{0.05}\text{Ace}_{0.05}/\text{Ti}$ catalysts displayed a NO conversion of 59.8, 73.0, and 55.8% at 150 °C, respectively.

Figure 3. NO conversion profiles of: (a) 20–30 wt.% $\text{Mn}_{0.75}\text{Ace}_{0.20}\text{Ni}_{0.05}\text{Ace}_{0.05}/\text{Ti}$ catalysts; (b) $\text{Mn}_{0.75}\text{Ace}_{0.20}\text{Ni}_{0.05}\text{Ace}_{0.05}/\text{Ti}$ catalysts with $\text{Mn}_{0.75-0.725}, \text{Fe}_{0.225-0.175}, \text{Ce}_{0.075-0.025}$ mole fractions.

Figure 3b shows the SCR activity of the 25 wt.% $\text{Mn}_{0.75}\text{Ace}_{0.20}\text{Ni}_{0.05}\text{Ace}_{0.05}/\text{Ti}$ catalyst with different Mn-Fe-Ce mole fractions. The highest NO conversion was attained at a Mn mole fraction of 0.75 and the lowest activity at a mole fraction of 0.725, indicating that the minimum Mn content should be 0.75. Maximum NO conversion was obtained at a Fe mole fraction of 0.20 followed by the mole fractions 0.175 and 0.225. Maximum NO conversion was obtained at a Ce mole fraction of 0.05 followed by 0.075 and 0.225. The $\text{Mn}_{0.75}\text{Ace}_{0.20}\text{Ni}_{0.05}\text{Ace}_{0.05}/\text{Ti}$, $\text{Mn}_{0.75}\text{Ace}_{0.20}\text{Ni}_{0.05}\text{Ace}_{0.05}/\text{Ti}$, $\text{Mn}_{0.75}\text{Ace}_{0.225}\text{Ni}_{0.025}\text{Ace}_{0.05}/\text{Ti}$, and $\text{Mn}_{0.75}\text{Ace}_{0.225}\text{Ni}_{0.025}\text{Ace}_{0.05}/\text{Ti}$ catalysts displayed NO conversions of 73.0, 65.2, 48.4, and 41.4 at 150 °C, respectively.

The effect of space velocity (mLg$^{-1}$h$^{-1}$) on the most active $\text{Mn}_{0.75}\text{Ace}_{0.20}\text{Ni}_{0.05}\text{Ace}_{0.05}/\text{Ti}$ catalyst is shown in Figure 4. Space velocity is an important factor to be considered in the catalyst design as well as to compare to catalysts in the open literature. The catalyst displayed a NO conversion of 98, 88 and 79%, respectively, at space velocities of 360,000, 450,000, and 600,000 mL g$^{-1}$ h$^{-1}$ at 200 °C. The fact that at the lowest space velocity, NO conversions of above 90% can be attained at temperatures above 200 °C indicates that unselective oxidation of NH$_3$ is not a major side reaction.

Figure 4. NO conversion profiles of the $\text{Mn}_{0.75}\text{Ace}_{0.20}\text{Ni}_{0.05}\text{Ace}_{0.05}/\text{Ti}$ catalyst at various space velocities.
The BET (Brunauer–Emmett–Teller) surface area, H₂-TPR, and NO oxidation results of the MnFe/Ti and MnFeCe/Ti catalysts are summarized in Table 2. The BET surface area of DT51-TiO₂ was 83 m²/g, while those of the MnFe/Ti and MnFeCe/Ti catalysts showed an increased surface area even with 25 wt.% active metal content. Thus, pore blockage of TiO₂ is unlikely and the active metal oxides are probably highly dispersed on the TiO₂ support. The increased surface area was due to increased microporosity compared to TiO₂ (see Figures S1 and S2, Supplementary Materials).

Table 2. Surface area, H₂-TPR (temperature-programmed reduction with hydrogen) and NO oxidation results.

| Catalyst                     | Surface Area (m²/g) | H₂ Consumption (µmol/g) | NO oxidation to NO₂ (%) * |
|------------------------------|---------------------|-------------------------|---------------------------|
| 25Mn₀.₇₅AceFe₀.₂₅Nit/Ti      | 95                  | 4120                    | 60                        |
| 25Mn₀.₇₅NitFe₀.₂₅Ace/Ti      | 91                  | 4004                    | 58                        |
| 25Mn₀.₇₅NitFe₀.₂₅Ace/Ti      | 100                 | 3996                    | 46                        |
| 25Mn₀.₇₅NitFe₀.₂₅Ace/Ti      | 100                 | 3972                    | 42                        |
| 25Mn₀.₇₅NitFe₀.₂₅Ace/Ti      | 102                 | 5040                    | 66                        |
| 25Mn₀.₇₅AceFe₀.₂₅NitCe₀.₀₅Ace/Ti | 96                | 4907                    | 56                        |

* NO oxidation to NO₂ at 300 °C.

Ease of reduction of metals oxides is known to be an indicator for favorable low temperature SCR activity [19]. The H₂ consumption profiles of the 25MnFe/Ti and 25MnFeCe/Ti catalysts are shown in Figure 5 and the integrated values (µmol/g) are summarized in Table 2. All 25MnFe/Ti catalysts showed almost similar reduction patterns. To distinguish the bimetallic reduction patterns of the MnFe/Ti catalysts, the reduction patterns of Fe/TiO₂ and Mn/TiO₂ were reported [19]. The Fe/TiO₂ catalyst reduced from Fe₂O₃ to Fe at 338 °C. The Mn/TiO₂ catalyst showed three peaks corresponding to step-wise reduction of MnO₂ to Mn₂O₃, Mn₂O₃ to Mn₃O₄, and Mn₃O₄ to MnO [19]. The 25MnFe/Ti materials exhibited only two peaks with the first (maximum at ≈255–270 °C) corresponding to the MnO₂ reduction, and the second one (maximum at ≈350–390 °C) could be due to the reduction of subsequent manganese oxide phases mixed with iron oxide. The 25Mn₀.₇₅AceFe₀.₂₅Ace/Ti and 25Mn₀.₇₅NitFe₀.₂₅Ace/Ti catalysts showed visible shoulder peaks at around 230 and 340 °C, and that of the 25Mn₀.₇₅AceFe₀.₂₅Nit/Ti and 25Mn₀.₇₅NitFe₀.₂₅Nit/Ti catalysts did not display visible shoulder peaks because of the broad nature of the reduction profiles. The origin of the shoulder peak toward lower temperature is unclear, but might be because of the presence of smaller, more easily reducible manganese oxide particles.

Figure 5. H₂-TPR (temperature-programmed reduction with hydrogen) profiles of (a) 25MnFe/Ti and (b) 25MnFeCe/Ti catalysts.
25Mn\textsubscript{0.75}AceFe\textsubscript{0.25}Nit/Ti catalyst was reduced at a relatively low temperature. Thus, the ease of reduction pattern and the dominating MnO\textsubscript{2} phase (first peak) for the 25Mn\textsubscript{0.75}AceFe\textsubscript{0.25}Nit/Ti catalyst seem to be the main contributors to the superior low temperature SCR activity.

The 25MnFeCe/Ti catalysts exhibited three reduction peaks, where the first two peaks can be assigned as similar to those of the MnFe/Ti catalysts and then the third reduction peak about 550 °C is due to the reduction of CeO\textsubscript{2} [25]. Most importantly, the 25Mn\textsubscript{0.75}AceFe\textsubscript{0.25}NitCe\textsubscript{0.05}Nit/Ti and 25Mn\textsubscript{0.75}AceFe\textsubscript{0.20}NitCe\textsubscript{0.05}Nit/Ti catalysts displayed a H\textsubscript{2} consumption of 5040 and 4907 µmol/g, respectively. This H\textsubscript{2} consumption, which is higher than for the 25MnFe/Ti catalysts, could be due to better dispersion of Mn, Fe, and Ce. The 25Mn\textsubscript{0.75}AceFe\textsubscript{0.20}NitCe\textsubscript{0.05}Ace/Ti catalyst was reduced at lower temperatures (≈10–15 °C) compared to the 25Mn\textsubscript{0.75}AceFe\textsubscript{0.20}NitCe\textsubscript{0.05}Nit/Ti catalyst. Thus, also in this case, the ease of reduction and the dominating MnO\textsubscript{2} phase (first reduction peak) in the 25Mn\textsubscript{0.75}AceFe\textsubscript{0.20}NitCe\textsubscript{0.05}Ace/Ti catalyst were the main reasons for the superior SCR activity at low temperature.

The X-ray powder diffraction (XRPD) patterns of the 25MnFe/Ti and 25MnFeCe/Ti catalysts are shown in Figure 6. The TiO\textsubscript{2} anatase phase was dominant in all catalysts and manganese oxide, iron oxide, and cerium oxides or other mixed phases of Mn, Fe, or Ce were not observed. This is a clear indication that active metal oxides are highly dispersed and/or in an amorphous state. To understand the amorphous state of the active metal oxides on the surface of the catalysts, thermal treatment at 400, 500, and 600 °C for 2 h was performed. It is anticipated that amorphous to crystalline phase transformation can happen by thermal treatment.

![Figure 6](image)

**Figure 6.** X-ray powder diffraction (XRPD) patterns of TiO\textsubscript{2} and the (a) 25MnFe/Ti and (b) 25MnFeCe/Ti catalysts.
SCR active. Further increase in calcination temperature resulted in the partial transformation of amorphous manganese oxide to crystalline manganese oxides (MnO₂ or Mn₂O₃). Overall, the SCR activity of the catalysts was in parallel to the amorphous to crystalline transformation of the catalysts as also reported by Kang and Tang et al. [26,27].

**Figure 7.** XRPD patterns of catalysts calcined at various temperatures: (a) 5MnAce/Ti; (b) 25Mn₀.₇₅AceFe₀.₂₅Nit/Ti; (c) 25Mn₀.₇₅AceFe₀.₂₀NitCe₀.₀₅Ace/Ti.

**Figure 8.** NO conversion profiles of catalysts calcined at various temperatures: (a) 5MnAce/Ti; (b) 25Mn₀.₇₅AceFe₀.₂₅Nit/Ti; and (c) 25Mn₀.₇₅AceFe₀.₂₀NitCe₀.₀₅Ace/Ti.
The impact of the calcination temperature and transformation of active oxides can also be studied in combination with H₂-TPR. The redox properties of the 5MnAce/Ti, 25Mn₀.₇₅AceFe₀.₂₅Nit/Ti, and 25Mn₀.₇₅AceFe₀.₂₀NitCe₀.₀₅Ace/Ti catalysts calcined at 400, 500, and 600 °C are shown in Figure 9. The 5MnAce/Ti catalyst showed three different reduction peaks, which correspond to stepwise reduction of MnO₂ to Mn₂O₃ (≈260 °C), Mn₂O₃ to Mn₃O₄ (≈360 °C), and Mn₃O₄ to MnO (≈460 °C) [19]. Increasing the calcination temperature from 400 to 600 °C, the 5MnAce/Ti catalyst shifted the first reduction peak to higher temperatures due to strong metal–support interactions [22], and the intensity of the second reduction peak was increased, which further indicates that the SCR active MnO₂ phase decreases and the Mn₂O₃ phase increases. The shifting of both reduction peaks to higher temperatures might be due to particle growth (sintering).

The 25Mn₀.₇₅AceFe₀.₂₀NitCe₀.₀₅Ace/Ti and 25Mn₀.₇₅AceFe₀.₂₅Nit/Ti catalysts displayed almost similar reduction patterns at 400 and 500 °C of calcination temperature, further indicating that Fe and Ce are inhibiting the phase transformation of MnO₂ to Mn₂O₃ and possibly particle growth (sintering). At 600 °C, the catalyst displayed a shift in the MnO₂ reduction peak to high temperatures and the intensity of the second reduction peak was increased. Thus, the combined presence of Fe and Ce on Mn/TiO₂ can increase the thermal stability.

The observed low temperature activity of Mn catalysts can also be explained by the NO to NO₂ oxidation ability as reported previously [15,18]. Table 2 shows the oxidation of NO to NO₂ on the 25Mn₀.₇₅Fe₀.₂₅Ti-DP and 25Mn₀.₇₅Fe₀.₂₅Ce₀.₀₅Ti-DP catalysts at 300 °C under wet conditions. All the catalysts displayed high NO to NO₂ conversion of 41.6 to 66%. The 25Mn₀.₇₅AceFe₀.₂₀NitCe₀.₀₅Ace/Ti and 25Mn₀.₇₅AceFe₀.₂₅Nit/Ti catalysts displayed the highest NO to NO₂ conversion. The observed NO oxidation is consistent with the
increased SCR activity of the catalysts, since partial conversion of NO into NO$_2$ is helpful to promote the fast SCR reaction, which is also known to go on at very low temperatures [28].

The surface composition as obtained by XPS (X-ray photoelectron spectroscopy) characterization is shown in Table 3. The 25Mn$_{0.75}$AceFe$_{0.25}$Nit/Ti and 25Mn$_{0.75}$AceFe$_{0.20}$NitCe$_{0.05}$Ace/Ti showed a surface Mn/Fe molar ratio of 2.08 and 1.30, respectively. Thus, it appears that the precursor/promoter combination has an influence on forming MnFe oxide species on the surface of the support. Importantly, the 25Mn$_{0.75}$AceFe$_{0.25}$Nit/Ti catalyst showed an O$_\alpha$ concentration of 50.1% of the total oxygen while the Ce promoted 25Mn$_{0.75}$AceFe$_{0.20}$NiCe$_{0.05}$Ace/Ti catalyst yielded 83.8%, respectively. High concentrations of chemisorbed oxygen have been reported to have a beneficial influence on the low-temperature SCR reaction [12,29] and is explained by an increased rate of NO to NO$_2$ oxidation [29]. Our XPS results showed a significantly higher concentration of more reactive surface oxygen (O$_\alpha$) in the 25Mn$_{0.75}$AceFe$_{0.20}$NiCe$_{0.05}$Ace/Ti catalyst than in the 25Mn$_{0.75}$AceFe$_{0.25}$Nit/Ti catalyst. This is reflected in the higher NO to NO$_2$ oxidation activity (66% vs. 60.4% conversion).

### 3. Experimental

#### 3.1. Catalyst Synthesis

TiO$_2$ in anatase form (DT-51 from Crystal Global with a S content of ≈1.25 wt%, SA = 87 m$^2$/g), γ-Al$_2$O$_3$ (Saint-Gobain, surface area of 256 m$^2$/g), and ZrO$_2$ (Saint-Gobain, surface area of 95 m$^2$/g) were used as support materials. Manganese(II) nitrate tetrahydrate (Mn(NO$_3$)$_2$·4H$_2$O, Aldrich), manganese (II) acetate tetrahydrate (CH$_3$COO)$_2$Mn·4H$_2$O, Aldrich), iron(III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O, Aldrich), iron(II) acetate (Fe(CO$_2$CH$_3$)$_2$, Aldrich), cerium (III) nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O, Aldrich), and Cerium (III) acetate hydrate (Ce(CH$_3$CO$_2$)$_3$·xH$_2$O, Aldrich) were used as precursors. The Mn/TiO$_2$, Mn-Fe/TiO$_2$, and Mn-Fe-Ce/TiO$_2$ catalysts were synthesized by deposition-precipitation. In deposition-precipitation (DP), the required amount of metal precursors (Mn, Fe, or Ce) and 1 g of support (TiO$_2$ or ZrO$_2$ or γ-Al$_2$O$_3$) was added to 10 mL demineralized water and mixed followed by the slow addition of ammonium carbamate solution (1 mol/L, Aldrich). The resulting slurry’s aqueous phase was slowly removed by evaporation with continuous stirring followed by 12 h of oven treatment at 120 °C and finally calcined for 2 h in air at 400 °C. The catalysts were designated with total metal loading, metal composition, and metal precursor as 20–30 wt.% Mn$_X$AceFe$_Y$NitCe$_Z$Ace/Ti, respectively. Here X, Y, and Z represent molar fractions of Mn, Fe, and Ce respectively (e.g., 25Mn$_{0.75}$AceFe$_{0.20}$NitCe$_{0.05}$Ace/Ti).

#### 3.2. Catalyst Characterization

##### 3.2.1. X-ray Powder Diffraction

X-ray powder diffraction (XRPD) was conducted with a Huber G670 instrument. CuKα radiation in steps of 0.02° was employed with a 2θ range of 2–60°. The Debye–Scherrer equation was used to calculate the crystallite sizes.

##### 3.2.2. Nitrogen Physisorption

BET surface areas were determined from N$_2$ physisorption measurements on about 100 mg at 77 K with a Micromeritics ASAP 2010 apparatus. The samples were pretreated at 200 °C for 1 h before the measurement.

##### 3.2.3. Chemisorption

H$_2$-TPR experiments were performed on a Micromeritics Autochem-II instrument with a reducing mixture (50 mL/min) consisting of 5% H$_2$ and balance Ar (Air Liquide)
from 60 to 550 °C (10 °C/min). The H₂ concentration in the effluent stream was monitored with a thermal conductivity detector (TCD).

3.2.4. X-ray Photoemission Spectroscopy

XPS measurements at room temperature were carried out with a Thermo scientific instrument. Al Kα radiation (1484.6 eV) was used and Au served as the standard for the instrument calibration. To minimize surface contamination, samples were outgassed in vacuum for 1 h in vacuum prior to the data acquisition. Deconvolution of spectra was performed using the Thermo Scientific Avantage Data system software.

3.3. Catalytic Activity Measurements

The SCR activity measurements were conducted in a fixed-bed reactor loaded with 50 mg of the fractionized (180–300 µm) catalyst at a flow rate of 300 NmL min⁻¹ (at room temperature) at atmospheric pressure. The concentrations at inlet were: NO = 1000 ppm, NH₃ = 1000 ppm, O₂ = 4%, and H₂O = 2.3% with He as the make up gas. The temperature was increased from 125 to 300 °C in steps of 25 °C while the NO and NH₃ concentrations were measured continuously with a Thermo Electron Model 17C chemiluminescense NH₃-NOx analyzer. The N₂O concentration was measured by GC (Shimadzu 14 B GC, poraplot column, TCD detection). The concentrations were measured after reaching steady state conversion (approximately 45 min at each temperature).

The NO oxidation to NO₂ measurements were performed in the same set up loaded with 200 mg of the fractionized (180–300 µm) catalyst at a flow rate of 300 NmL min⁻¹ (at room temperature). The inlet concentrations were: NO = 500 ppm, O₂ = 4.5% and H₂O = 2.3% with He as balance gas. During the experiments the temperature was increased in steps of 50 °C from 150 to 350 °C while the NO and NO₂ concentrations were measured with a Thermo scientific UV–Vis spectrophotometer (Evolution 220).

4. Conclusions

A range of precursor combinations in deposition-precipitation synthesis were tested on highly active low temperature SCR of NO with NH₃ catalysts. Among the three supports (TiO₂, ZrO₂, and Al₂O₃) and two precursor combinations (nitrate vs. acetate), a monometallic 5MnAce/Ti catalyst showed good low temperature SCR activity. Among the bimetallic catalysts, the 25Mn₅⁰Fe₂⁰₂⁵Ni₇/Ti catalysts showed better low temperature SCR activity, and the trimetallic 25Mn₅⁰Fe₂⁰₂⁰Ce₃₅Ace/Ti catalyst showed the best low temperature SCR activity, respectively. The addition of Fe, and especially Ce, not only enhances the activity, but also the thermal stability by hindering the transformation of finely dispersed, easily reducible amorphous manganese oxide phases into larger, less easily reducible, and more crystalline particles as evidenced by H₂-TPR and XRD. Fe and Ce promoted catalysts were shown by XPS to contain large amounts of surface active oxygen, further corroborating the H₂-TPR and XRD results. This form of oxygen can enhance the oxidation of NO to NO₂, as shown by NO oxidation measurements, and can promote fast-SCR and hence the overall activity. Furthermore, Ce lowers the selectivity toward N₂O, possibly by enhancing the rate of reaction of activated NH₃ with NO to N₂, thus making it unavailable for over-oxidation, which can lead to N₂O formation.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4344/11/2/259/s1, Figure S1: Adsorption/desorption isotherms of 25MnFe/Ti and 25MnFeCe/Ti catalysts with TiO₂ support. Figure S2: Cumulative surface area as a function of the BJH (Barrett-Joyner-Halenda) pore width (from adsorption branch) of the 25MnFe/Ti, 25MnFeCe/Ti catalysts and TiO₂ support.
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References

1. Bosch, H.; Janssen, F. Formation and control of nitrogen oxides. Catal. Today 1988, 2, 369–379.
2. Parvulescu, V.I.; Grange, P.; Delmon, B. Catalytic removal of NO. Catal. Today 1998, 46, 233–316. [CrossRef]
3. Busca, G.; Lietti, L.; Ramis, G.; Berti, F. Chemical and mechanistic aspects of the selective catalytic reduction of NOx by ammonia over oxide catalysts: A review. Appl. Catal. B 1998, 18, 1–36. [CrossRef]
4. Alemany, L.J.; Lietti, L.; Ferlazzo, N.; Forzatti, P.; Busca, G.; Giamello, E.; Bregani, F. Reactivity and physicochemical characterization of V2O5-WO3/TiO2 De-NOx catalysts. J. Catal. 1995, 155, 117–130.
5. Heck, R.M. Catalytic abatement of nitrogen oxides-stationary applications. Catal. Today 1999, 53, 519–523. [CrossRef]
6. Due-Hansen, J.; Boghosian, S.; Kustov, A.; Fristrup, P.; Tsilomelekis, G.; Stähli, K.; Christensen, C.H.; Fehrmann, R. Vanadia-based SCR catalysts supported on tungstated and sulfated zirconia: Influence of doping with potassium. J. Catal. 2007, 251, 459–473. [CrossRef]
7. Putluru, S.S.R.; Jensen, A.D.; Riisager, A.; Fehrmann, R. Heteropoly acid promoted V2O5/TiO2 catalysts for NO abatement with ammonia in alkali containing flue gases. Catal. Sci. Technol 2011, 1, 631–637. [CrossRef]
8. Putluru, S.S.R.; Kristensen, S.B.; Due-Hansen, J.; Riisager, A.; Fehrmann, R. Alternative alkali resistant deNOx catalysts. Catal. Today 2012, 184, 192–196. [CrossRef]
9. Singorejdo, L.; Korver, R.; Kapteijn, F.; Moulijn, J. Alumina Supported Manganese Oxides for the Low-Temperature Selective Catalytic Reduction of Nitric-Oxide with Ammonia. Appl. Catal. B Environ. 1992, 1, 297–316. [CrossRef]
10. Smirniotis, P.G.; Peña, D.A.; Uphade, B.S. Low-temperature selective catalytic reduction (SCR) of NO with NH3 by using Mn, Cr, and Cu oxides supported on Hombikat TiO2. Angew. Chem. Int. Ed. 2001, 40, 2479–2482. [CrossRef]
11. Long, R.Q.; Yang, R.T.; Chang, R. Low temperature selective catalytic reduction (SCR) of NO with NH3 over Fe-Mn based catalysts. Chem. Commun. 2002, 5, 452–453. [CrossRef]
12. Wu, Z.; Jiang, B.; Liu, Y. Effect of transition metals addition on the catalyst for manganese/titania for low-temperature selective catalytic reduction of nitric oxide with ammonia. Appl. Catal. B 2008, 79, 347–355. [CrossRef]
13. Roy, S.; Viswanath, B.; Hegde, M.S.; Madras, G. Low-temperature selective catalytic reduction of NO with NH3 over Ti0.9M0.1O2-δ (M= Cr, Mn, Fe, Co, Cu). J. Phys. Chem. C 2008, 112, 6002–6012. [CrossRef]
14. Qi, G.; Yang, R.T. Low-temperature selective catalytic reduction of NO with NH3 over iron and manganese oxides supported on titania. Appl. Catal. B Environ. 2003, 44, 217–225. [CrossRef]
15. Wu, S.; Yao, X.; Zhang, L.; Cao, Y.; Zou, W.; Li, L.; Ma, K.; Tang, C.; Gao, F.; Dong, L. Improved low temperature NH3-SCR performance of FeMnTiOx mixed oxide with CTAB-assisted synthesis. Chem. Commun. 2015, 51, 3470–3473. [CrossRef]
16. Qi, G.; Yang, R.T.; Chang, R. MnOx-Co2O3 mixed oxides prepared by co-precipitation for selective catalytic reduction of NO with NH3 at low temperatures. Appl. Catal. B Environ. 2004, 51, 93–106. [CrossRef]
17. Shang, T.; Hui, S.; Niu, Y.; Liang, L.; Liu, C.; Wang, D. Effect of the addition of Ce to MnOx/TiO2 catalyst on reduction of NO2 in low-temperature SCR. Asia Pac. J. Chem. Eng. 2014, 9, 810–817. [CrossRef]
18. Jin, R.; Liu, Y.; Wang, Y.; Cen, W.; Wu, Z.; Wang, H.; Weng, X. The role of cerium in the improved SO2 tolerance for NO reduction with NH3 over Mn-Ce/TiO2 catalysts at low temperature. Appl. Catal. B Environ. 2014, 148–149, 582–588. [CrossRef]
19. Putluru, S.S.R.; Schill, I.; Jensen, A.D.; Siret, B.; Tabaries, F.; Fehrmann, R. Mn/TiO2 and Mn-Fe/TiO2 catalysts synthesized by deposition precipitation-promising for selective catalytic reduction of NO with NH3 at low temperatures. Appl. Catal. B Environ. 2015, 165, 628–635. [CrossRef]
20. Kapteijn, F.; Vanlangeveld, A.D.; Moulijn, J.A.; Andreini, A.; Vuurman, M.A.; Turek, A.M.; Jehng, J.M.; Wachs, I.E. Alumina-Supported Manganese Oxide Catalysts. J. Catal. 1994, 150, 94–104. [CrossRef]
21. Li, J.; Chen, J.; Ke, R.; Luo, C.; Hao, J. Effects of precursor on the surface Mn species and the activities for NO reduction over MnOx/TiO2 catalysts. Catalum. Commun. 2007, 8, 1896–1900. [CrossRef]
22. Peña, D.A.; Uphade, B.S.; Smirniotis, P.G. TiO2-supported metal oxide catalysts for low-temperature selective catalytic reduction of NO with NH3: I. Evaluation and characterization of first row transition metals. J. Catal. 2004, 221, 421–431. [CrossRef]
23. Huang, Z.; Gu, X.; Wen, W.; Hu, P.; Makkee, M.; Lin, H.; Kapteijn, F.; Tang, X. A “smart” hollandite deNOx catalyst: Self-protection against alkali poisoning. *Angew. Chem. Int. Ed.* **2013**, *52*, 660–664. [CrossRef]

24. Smirniotis, P.G.; Sreekanth, P.M.; Peña, D.A.; Jenkins, R.G. Manganese oxide catalysts supported on TiO₂, Al₂O₃, and SiO₂: A comparison for low-temperature SCR of NO with NH₃. *Ind. Eng. Chem. Res.* **2006**, *45*, 6436–6443. [CrossRef]

25. Thirupathi, B.; Smirniotis, P.G. Co-doping a metal (Cr, Fe, Co, Ni, Cu, Zn, Ce, and Zr) on Mn/TiO₂ catalyst and its effect on the selective reduction of NO with NH₃ at low-temperatures. *Appl. Catal. B Environ.* **2011**, *110*, 195–206. [CrossRef]

26. Kang, M.; Park, E.D.; Kim, J.M.; Yie, J.E. Manganese oxide catalysts for NOx reduction with NH₃ at low temperatures. *Appl. Catal. A Gen.* **2007**, *327*, 261–269. [CrossRef]

27. Tang, X.; Hao, J.; Xu, W.; Li, J. Low temperature selective catalytic reduction of NOx with NH₃ over amorphous MnOx catalysts prepared by three methods. *Catal. Commun.* **2007**, *8*, 329–334. [CrossRef]

28. Iwasaki, M.; Shinjoh, H. A comparative study of “standard”, “fast” and “nO₂” SCR reactions over Fe/zeolite catalyst. *Appl. Catal. A Gen.* **2010**, *390*, 71–77. [CrossRef]

29. Shen, B.; Liu, T.; Zhao, N.; Yang, X.; Deng, L. Iron-doped Mn-Ce/TiO₂ catalyst for low temperature selective catalytic reduction of NO with NH₃. *J. Environ. Sci.* **2010**, *22*, 1447–1454. [CrossRef]