Unraveling the Structure and Role of Mn and Ce for Selective Catalytic Reduction of NO_x in Application-Relevant Catalysts and Conditions

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**Unraveling the Structure and Role of Mn and Ce for Selective Catalytic
Reduction of NO_x in Application-Relevant Catalysts and Conditions**

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14 **Abstract**

15 Mn-based oxides are promising catalysts for the selective catalytic reduction (SCR) of NO_x with NH₃ at
16 temperatures below 200 °C. There is a general agreement that combining Mn with another metal
17 oxide, such as CeO_x improves catalytic activity. However, to date, there is an unsettling debate on the
18 role of Ce as Mn promoter on the SCR reaction. To solve this, here we have systematically studied the
19 effect Ce by preparing, characterizing and testing around 30 catalysts aiming for a well-controlled
20 homogeneous dispersion of the metal oxides. Our results show that, at low-temperature SCR
21 conditions, the intrinsic activity of the Mn active sites is not positively affected by Ce species in
22 intimate contact. In fact, the results suggest that Ce is electronically interacting with Mn and
23 decreasing the active-site average activity. To confirm our findings, activities reported in literature
24 were surface-area normalized and the analysis do not support an increase in activity by Ce addition.
25 Therefore, we can unequivocally conclude that the beneficial effect of Ce is textural, increasing
26 catalyst surface area and therefore the total number of active sites. Besides, addition of Ce is
27 increasing N₂ selectivity as it suppresses second-step oxidation reactions and thus N₂O formation by
28 structurally diluting the MnO_x active sites. Therefore, the textural promoting effect still makes Ce an
29 interesting additive for Mn catalysts.

30

Introduction

The selective catalytic reduction (SCR) of environmentally harmful nitric oxide (NO) with ammonia (NH_3) is a well-known and established technology for the denitrification of exhaust gases from stationary (power plant) and mobile (e.g. lean burn engines) sources.¹⁻³ However, the more stringent global legislations and the relatively low exhaust temperatures of more efficient engines and low-load engine operations require the search for more efficient catalytic systems. For example, In Euro 6 stage the European Union legislative authorities have tightened the limits of nitrogen oxides being emitted from diesel cars (from 180 mg NO_x/km in Euro 5 to 80 mg NO_x/km in Euro 6).⁴ A wide variety of catalytic systems based on metal-containing zeolites and mixed metal oxides have been investigated in this reaction. The introduction of Cu-exchanged small pore molecular sieves such as Cu-SSZ-13 and Cu-SAPO-34 have been a revolutionary technology for SCR applications⁵ and have an optimal performance between 200 – 450 °C.⁶⁻⁸ Among mixed metal oxides, $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ catalysts give more than 90 % NO conversion at gas hourly space velocities (GHSV) of 60000 – 90000 h^{-1} between 250 – 400 °C.⁹⁻¹³ However, all these systems fall short of providing sufficient performance at temperatures below 200 °C. Catalyst operating at lower temperatures are imperative in mobile applications due to engine cold start¹⁴ and new advances in low-temperature combustion¹⁵. In this respect, manganese-containing mixed metal oxides exhibit excellent catalytic activity in the $\text{NH}_3\text{-SCR}$ reaction operating at temperatures below 200 °C, and therefore is of particular interest as a potential low-temperature component in $\text{NH}_3\text{-SCR}$.¹⁶⁻²⁰

Typically, Mn-based catalysts are prepared by impregnation or homogeneous precipitation methods with other metal oxides, such as Ti and Ce oxides, that act as support, dopants or promoters. During the last decades, the role of the different components on the catalytic activity and selectivity have been debated extensively³. Mn catalytic activity originates from its excellent redox ability at low temperatures. The importance of specific surface area, dispersion and oxidation state of the different Mn oxides have been highlighted²¹⁻²³. TiO_2 is considered a metal oxide support providing optimal dispersion of Mn active species, surface area, thermal stability and Lewis acid sites to adsorb NH_3 ^{24, 25}.

For Ce and other transition metal, there is no clear consensus on their role on the catalytic reaction. The promotional effect is often explained by an improvement of the catalytic redox cycles by intimate contact of the active Mn oxides and the promoters²⁶⁻²⁸. Among the transition metals, Ce is widely used and probably one of the most promising promoters³. In binary MnCe systems, the addition of Ce was reported to improve the conversion levels compared to individual Mn oxides^{29, 30}. This promotional effect is generally explained by an enhancement of the redox functionality, which is proven by the easier reduction of Ce and/or Mn during temperature-programmed reduction experiments³¹. Baiker et al. also postulated that binary MnCe oxides have a higher adsorption of NO and NH₃, which promotes catalytic activity³². In ternary MnCeTi oxides, the improvement of activity by Ce is also frequently explained by an increase of the Mn redox properties^{31, 33-35}. In contrast, other studies suggest that the Mn-Ce electronic interaction decrease the activity of Mn species for NO conversion³⁶ by a reduction of the Mn⁴⁺/Mn³⁺ ratio. On the basis of the measured surface areas, binary MnCe^{29, 30, 32} and tertiary MnCeTi^{31, 33, 36-38} systems show better textural properties when Ce is added, but this is rarely discussed as a main promoting effect.

To resolve this unsettled dilemma, we studied the structure and catalytic performance of Mn, Ce and Ti mixed-oxide catalysts with a wide range of metal-oxide compositions. The catalysts were prepared by a homogeneous precipitation method designed to obtain mixed oxides with amorphous structure and a homogeneous dispersion of the distinct metal oxides. More specifically, 30 catalysts were systematically synthesized with different Mn, Ce and Ti compositions. To verify the formation of an amorphous and homogeneous mixed oxide, we have chosen a multi-technique approach combining XRD, electron microscopy and high-resolution X-ray photoelectron spectroscopy. The low temperature NH₃-SCR performance of all the catalysts was investigated under relevant conditions encountered in a car exhaust.

Catalyst synthesis, structure and metal-oxide spatial distribution.

After synthesis of the catalysts, we aim to characterize their structure and chemical properties by a multi-pronged approach. The crystalline structure of the catalysts was studied by powder X-ray diffraction, and crystallite sizes were calculated from diffraction peaks integral breadth using the Scherrer equation. The results are summarized in the ternary diagram plotted in Fig. 1 and the detailed diffraction patterns and crystallite size analysis are in the Supplementary information (Supplementary Fig. 2, Supplementary Fig. 3 and Supplementary Table 2).

Fig. 1. Ternary phase diagram of the synthesized MnCeTiOx catalyst samples. The colored areas highlight groups of samples with similar crystal phases, measured by XRD.

The binary catalysts have a certain degree of crystallinity and show reflection lines of fluorite CeO₂ structure in the CeTi and MnCe oxides and rutile TiO₂ in the MnTi oxides. MnO_x crystalline phases, α -

Mn₂O₃ (Bixbyite), Mn₅O₈, Mn₃O₄ (Hausmannite) and MnO(OH) (Groutite) are observed on the MnCe oxides, whereas binary MnTi samples display weak and broad reflections from MnO_x phases, indicating nano-crystallites below 3-4 nm, most likely on the TiO₂ surface. The existence of mono-component metal oxide crystalline phases is an indisputable proof that the preparation method is not successful for the synthesis of well-mixed oxides in binary systems. In sheer contrast to the binary systems, the diffraction patterns of most of the ternary systems show featureless diffraction patterns indicating the amorphous nature of the samples (Supplementary Fig. 3). Only a few samples with high Ti (Mn_{0.08}Ce_{0.13}Ti_{0.79}) or Ce (Mn_{0.07}Ce_{0.55}Ti_{0.37} and Mn_{0.11}Ce_{0.48}Ti_{0.41}) content display reflections from anatase TiO₂ or fluorite CeO₂, respectively. This suggest that the third metal component facilitates the formation of a ternary amorphous phase, which is the first step on obtaining a homogeneous mixed oxide. Very importantly, the effect of Ce is crucial in the formation of an amorphous phase, as small amounts of such a component inhibits the formation of crystalline phases, as can be observed in the low edge of the ternary diagram in Fig. 1.

The bulk and surface composition of the catalysts were compared by using Inductive Coupled Plasma (ICP) and high-resolution X-ray Photoelectron Spectroscopy (XPS), respectively (Supplementary Table 1). The bulk chemical composition of the catalysts is comparable with the theoretical composition, with a slight deviation to lower Mn concentrations, which suggests that not all the Mn is precipitated during synthesis. One plausible explanation is the formation of soluble Mn complexes with ammonium ligands, which are less prone to hydrolysis-condensation reactions³⁹. Those are expected to remain in the supernatant during the washing by centrifugation, thus decreasing the final Mn content on the catalyst. The bulk composition was compared to the surface composition of selected samples by XPS. For the Mn-Ti binary, there is an enrichment of Mn on the surface, in line with the hypothesis that Mn is supported on TiO₂. For the ternary systems, the results show that surface compositions are similar to bulk compositions, with some of the samples displaying a modest enrichment of Mn and Ce on the surface.

121 To further investigate the structure, metal oxide distribution and local composition of the catalysts,
122 we performed a high-resolution electron microscopy study. A representative transmission electron
123 microscopy (TEM) image of a binary MnTi Sample ($\text{Mn}_{0.37}\text{Ce}_{0.00}\text{Ti}_{0.63}$) is shown in Supplementary Fig. 4.
124 We observed nanosized and crystalline TiO_2 particles decorated with layers of amorphous material.
125 High-angle annular dark-field (HAADF) STEM imaging and elemental mappings computed from energy-
126 dispersive X-ray spectroscopy (EDX) data, presented in Supplementary Fig. 5, reveal that Mn is well
127 dispersed on the TiO_2 particles. In contrast, TEM images of a representative MnCeTi ternary system,
128 in Fig. 2a and b, corroborate the existence of a purely amorphous system. The structural features
129 resemble an agglomeration of shapeless nanoparticles forming a random porous structure. Annular
130 dark-field (ADF) STEM imaging and elemental mapping computed from EELS data confirm the
131 homogeneous distribution of Mn, Ce and Ti metals over individual catalyst particles.

Fig. 2. (a and b) Representative HRTEM images of the $\text{Mn}_{0.14}\text{Ce}_{0.13}\text{Ti}_{0.74}$ oxide catalyst. ADF-STEM images and elemental mappings of the same catalyst at (a-d) low and (e-i) high magnification.

All the results strongly confirm that our synthesis route renders a homogeneous distribution of all the metal atoms in the ternary system and indicate that our synthesis method is effective for the preparation of ideal perfectly-mixed ternary metal oxides. From the characterization measurements conducted, we illustrate the structure of the MnTi binary and the MnCeTi ternary catalysts in Fig. 3.

Fig. 3. Schematic representation of a) MnTi binary catalysts where amorphous layers of Mn oxide active are on the surface of crystalline TiO_2 and b) MnCeTi ternary catalysts where the metal oxides are amorphous and well mixed.

Impact of metal oxide composition on catalyst textural properties, oxide reducibility and

speciation. The specific surface areas of the discrete catalysts are presented in the ternary diagram in Fig. 4 and in supplementary Table 3.

Fig. 4. Ternary diagrams showing the Influence of catalyst composition on BET surface area.

150

151 The catalyst materials have a clear type IV isotherm, with an H1 loop characteristic of mesoporous
152 coming from the agglomeration of the metal-oxide nanoparticles. Clearly, Ce content has a significant
153 impact on specific surface areas of the ternary catalysts. The addition of Ce plays a key role as
154 structural promotor increasing the surface area from 108 to 245 m²/g when Ce content increases from
155 0 to 20 mol%. A further increase in Ce has a negative impact and surface areas drop down to 62 m²/g
156 when Ce concentration reaches 55 mol%, similar to previous studies on Ce-Ti⁴⁰, Mn-Ce⁴¹ binary
157 systems and Mn-Ce-Ti ternary systems⁴². Comparing the XRD and BET data, the increase of surface
158 area is strongly correlated with the formation of amorphous structures.

159 To investigate the redox properties of the materials, temperature-programmed reduction (TPR)
160 experiments with H₂ were performed. Overall, the reduction peak at 200-450 °C is attributed to the
161 reduction of Mn⁴⁺ and Mn³⁺ species to Mn²⁺^{43, 44}, whereas the main reduction peak at 550-650 °C is
162 ascribed to the reduction of Ce⁴⁺ to Ce³⁺ in a mixed oxide phase⁴⁵⁻⁴⁷. The difference in the TPR of pure
163 CeO₂, plotted on supplementary Fig. 6, confirms that Ce is well-mixed and strongly interacting with
164 Mn and Ti. The samples containing a low Mn/Ce molar ratio, plotted in Fig. 5a, show a monotonic
165 decrease in the reduction temperature of Ce when Mn content increases. According to literature
166 reports, the main parameters influencing the reduction temperature are specific surface area and the
167 presence of other metals in intimate contact⁴⁸. In this case, the surface area of the binary Ce-Ti system
168 is higher than the Mn-contained samples shown in Fig. 5a. Therefore, changes in the reduction
169 temperature are unrelated to specific surface area and can be rationalized as a consequence of the
170 close proximity of Mn and Ce species, which improves the reducibility and thus the redox properties
171 of Ce. The TPR of samples containing high amount of Mn are shown in Fig. 5b. For the binary Mn-Ti
172 samples, two main peaks from Mn reduction (289-306 °C and 341-408 °C) are observed. Addition of
173 Ce in the catalyst formulation has a strong impact on the TPR profiles: the low temperature peak
174 strongly decreases with small amounts of Ce and the high temperature contribution shifts to higher

temperatures with increasing Ce content (see also Supplementary Fig. 7). We surmise that the changes in the TPR profiles probably result from the lower reducibility of the Mn species in close contact with Ce.

Fig. 5. Temperature-programmed reductions with H₂ of selected samples with a) a low Mn/Ce molar ratio and b) a high Mn/Ce molar ratio. The low-temperature evolution (in purple) is related to the reduction of MnO_x phases whereas the high-temperature (in cream) is related to CeO₂ reduction.

To gain more nuanced insight into the effect of Ce to the catalyst redox properties, a detailed high-resolution XPS study was performed. Oxidation states of Mn were rigorously fitted from a set of Gaussian-Lorentzian components per oxidation state, due to the multiplet splitting between the unpaired electrons in Mn 2+, 3+ and 4+. The set of components of the discrete oxidation states were obtained from measurements of pure MnO, Mn₂O₃ and MnO₂ oxides and the results were compared with previously reported measurements⁴⁹. More experimental details can be found on the supplementary information and supplementary Fig. 8. The Mn(2p_{3/2}) spectra from selected samples show a high amount of Mn³⁺ species in the binary Mn-Ti catalysts, whereas a combination of Mn⁴⁺ and Mn²⁺ dominates the spectra of ternary samples (see supplementary table 5). There is no clear consensus in the literature on the effect of Ce on the Mn oxidation state. Whilst several authors found an increase in Mn³⁺ species with the addition of Ce^{31, 35, 36}, Feng et al. observed a slight reduction in Mn³⁺³⁸, and others found no clear correlation^{50, 51}. The origin of the discrepancy could be related to the complexity on the analysis of the Mn (2p_{3/2}) spectra and the different structure of the prepared catalysts. In order to improve the confidence in our results, average Mn oxidation states were calculated from the XPS and TPR and gave comparable results (see supplementary Table 6), which validates our XPS deconvolution method and confirms that the addition of Ce decreases the average Mn oxidation state. Based on our structural characterization results, we speculate that the reduction in the average Mn oxidation state is due to the existence of Ce species in close proximity to Mn. This might explain the shifting of TPR profile to high temperature after introducing Ce into the MnTi system.

Role of Mn and Ce on NO reduction at low temperature. Next, we inspected the activity of the different samples in the selective catalytic reduction of NO with NH₃ at 150 °C. During the activity measurements, there was no NO₂ formation and the only products were N₂ and N₂O. Activity plot with the amount of Mn shows a close-to-zero intercept of the ordinate, indicating that Mn oxides are the

most important species in catalytic performance (Supplementary Fig. 9). Up to 60% of Mn, there is a modest correlation of the increase of activity with the increase in Mn content. However, the results revealed that no evident trend is observed when Mn is above 60% and strongly suggest that Mn content is not the only factor determining catalytic activity.

To unravel the effect of the distinct metal oxides, we re-examined the catalytic performance by surface area normalization of the activity. Specific activities (ml of NO converted per m² and per min) were plotted as a function of Mn content in Fig. 6. For the individual Mn and the binary Mn-Ti samples, a clear linear dependency of the measured specific activities with the Mn content is observed. The Mn-Ce-Ti ternary systems has also a pseudolinear correlation with the Mn content but with a lower slope. The Mn surface enrichment for the Mn-Ti catalysts observed by XPS (Table S1) can insufficiently explain the almost twofold increase in specific activity. Therefore, we infer that MnO_x species in the individual Mn and binary Mn-Ti catalysts have similar activity, and those are more active than in the Mn-Ce-Ti ternary system. The results are also in line with the higher reduction temperature of manganese species observed in the TPR data of Mn-Ce-Ti ternary systems.

Fig. 6. Surface-specific activities for the NO reduction at 150 °C plotted as a function of the Mn content on the catalysts. The blue dots correspond to the ternary Mn-Ce-Ti catalysts. The red dots are from the binary Mn-Ti and the individual Mn catalysts. Red and blue trendlines were added to guide the eyes.

To assess the implication of the different MnO_x species on catalytic performance, the normalized activities with the distinct Mn surface species (Mn⁴⁺, Mn³⁺, Mn²⁺ and total Mn) were constructed in Supplementary Fig. 10. The plots show an increase in activity with the amount of Mn⁴⁺ and Mn³⁺ species, however there are no direct evidences that the Mn²⁺ species are promoting catalyst activity, in line with previous reports⁵². Hence, the increase in the Mn²⁺ content in the samples containing Ce could, to a certain extent, explain the lower specific activity of those samples. In addition, the substantial effect of Ce on the TPR profiles, shifting reduction peaks of Mn⁴⁺ and Mn³⁺ to higher temperatures, indicates that other interactions of Mn⁴⁺ and Mn³⁺ with Ce species can be responsible for the lower specific activity.

We further investigated the nature of the oxygen species in the solid catalyst, which has been suggested to have a significant impact on SCR activity, more specifically on the oxidation reactions^{53, 54}. The reactivity of oxygen species on the catalyst was investigated by monitoring the formation of N₂O during NH₃-TPD experiments. In these experiments, N₂O is formed in the range of 140 to 440 °C via the oxidation of ammonia with active oxygen species on the catalyst surface. The plots in supplementary Fig. 11. shows that NO activities at 150 °C are correlated to the amount of evolved N₂O during NH₃-TPD experiments. pointing to the direct key role of the active oxygen in overall reaction mechanism at low temperature. Since the NO activity is related to Mn content, we can infer that those active oxygen species are related to Mn species.

The effect of Ce on the Mn activity has been previously reported in the literature with inconsistent findings. For example, Liu et al. proposed a positive effect of Ce and Ti in activity by a dual redox cycle consisting of $\text{Mn}^{4+} + \text{Ce}^{3+} \leftrightarrow \text{Mn}^{3+} + \text{Ce}^{4+}$ and $\text{Mn}^{4+} + \text{Ti}^{3+} \leftrightarrow \text{Mn}^{3+} + \text{Ti}^{4+}$ cycles³¹. A different explanation of the beneficial effect of Ce was proposed by Yang et al., based on a mechanistic study using *in-situ* FTIR spectroscopy. The authors suggested that MnO_x species show a faster rate for the conversion of NO to nitrate or nitrite, whereas CeO₂ mainly provides adsorption sites resulting in nitrites species²⁹. In line with our results, Wu et al. also observed a negative effect of Ce in the activity in ternary Mn-Ce-Ti compared to binary Mn-Ti. However, these authors explained the negative effect of Ce by a reduction in the Mn⁴⁺/Mn³⁺ ratio³⁶. In order to resolve the origin of these contradicting findings, our results were contrasted with previously reported ones after surface-area normalization of the activity data. These data are shown in Supplementary Table 8. The analysis shows that when the activities are surface-area normalized, there is no positive effect of the addition of Ce on the specific Mn activity, which validates our experimental results. Although this analysis is incomplete due to our lack of knowledge on several parameters, such as Mn surface composition, oxidation states, degree of interaction between the different oxide species, etc., there is no apparent trend pointing to an increase in activity by Ce addition. Therefore, we propose that Ce is not improving the catalytic

properties of Mn species at low reaction temperatures and that the only promotional effect is purely structural due to an increase in catalyst surface area.

When looking at the catalytic performance at higher temperatures, the role of Ce is clear. Supplementary Fig. 12 shows NO_x conversion of selected samples with increasing the amount of Ce. The activity data of all catalyst samples can be found in supplementary table S7. The binary MnTi catalysts has the highest activity at low temperatures, but the catalytic performance drastically drops at temperatures higher than 250 °C due to the unselective oxidation of NH₃ to NO_x. The addition of Ce drops the conversion at low temperatures, but promotes NO_x conversion at temperatures higher than 250 °C, widening the operational temperature window of the catalyst materials. Understanding this effect lies beyond the scope of our investigations as other parameters, such as close proximity of the redox and acidic functions, may govern the reaction at high temperatures⁵⁶.

Role of Mn and Ce on N₂O selectivity at low temperature

Finally, the N₂O formation at low temperature was investigated on all the samples. Possible effects of conversion on N₂O selectivity were ruled out by inspecting the N₂O selectivity plot as function of conversion in Supplementary Fig. 13. In general, the N₂O formed over MnO_x and binary Mn-Ti catalysts is significantly higher than in the Mn-Ce-Ti ternary systems. For a deeper analysis of the selectivity results, the surface-specific formation of N₂O of selected samples was plotted in Fig. 7 as function of the Mn surface density calculated from the XPS measurements. The results clearly show an exponential increase of the N₂O formation at 150 °C with the Mn surface density, indicating that N₂O formation obeys a higher-than-one-order dependence in Mn. Our characterization and NO_x activity measurements pointed to an interaction of Ce with Mn, leading to a decrease in the Mn activity. This can definitely play a role in the lower N₂O activity but does not fully describe the Mn order dependence. A plausible explanation of this behavior is that more than one Mn active species in close proximity must participate in the kinetic formation of N₂O. According to literature, two main reaction

mechanisms explain the formation of N_2O at low temperature⁵⁷: one based on a Langmuir-Hinshelwood mechanism where NO is oxidized to NO_3^- species that react with NH_4^+ to give N_2O , and the other is an Eley-Rideal mechanism resulting from the oxidative dehydrogenation of NH_3 to NH species that react with NO to yield N_2O . A mechanistic study on the formation of N_2O is beyond the goal of this work, but both proposed mechanisms are based on multistep oxidation of NO and/or NH_3 . Therefore, we postulate that the formation of N_2O requires the participation of at least two Mn active sites and that is promoted by neighboring Mn active sites. The homogeneous composition of the ternary Mn-Ce-Ti dilutes the Mn species on the catalyst surface and inhibits subsequent oxidation steps by breaking up the MnOx ensembles. This mechanism is schematically depicted in Fig. 8. Besides the dilution effect, the addition of Ce could also decrease the activity of surface oxygen observed by a suppressed N_2O formation in the NH_3 -TPD.

Fig. 7. surface-specific N_2O rates at 150 °C as a function of the Mn surface density. Samples from lower to higher Mn surface density: $\text{Mn}_{0.08}\text{Ce}_{0.55}\text{Ti}_{0.37}$, $\text{Mn}_{0.14}\text{Ce}_{0.13}\text{Ti}_{0.74}$, $\text{Mn}_{0.21}\text{Ce}_{0.25}\text{Ti}_{0.54}$, $\text{Mn}_{0.30}\text{Ce}_{0.19}\text{Ti}_{0.51}$, $\text{Mn}_{0.36}\text{Ce}_{0.04}\text{Ti}_{0.60}$, $\text{Mn}_{0.35}\text{Ce}_{0.00}\text{Ti}_{0.65}$. The blue line is a guide to the eye suggesting an exponential-type trend.

To rule out the effect of the amount of ammonia adsorbed on the catalysts on N₂O selectivity, NH₃-TPD measurements were performed and the total number of acid sites, obtained from the total amount of ammonia adsorbed, was plotted as a function of Ce content (Supplementary Fig. 13). The total acidity of all the samples was also plotted in the ternary diagram in Supplementary Fig. 14. The total acidity is around 1.1 $\mu\text{mol}/\text{m}^2$ up to 20% Ce and then monotonically increases up to around 2.5 $\mu\text{mol}/\text{m}^2$. Owing to the fact that the inhibiting of N₂O formation is observed in catalysts with Ce content below 20%, we can exclude the role of the number of acid sites on the N₂O formation.

Fig. 8. A schematic representation of the reaction mechanism in a) a MnTi binary catalyst where the close proximity of MnO_x species promote the formation of N₂O and b) a MnCeTi ternary catalyst in which the well-mixed amorphous structure promotes the spacing of MnO_x species and therefore reduces the formation of N₂O.

Concluding, our research results add new insight into our understanding of Mn catalysts for low-temperature NH₃-SCR applications and provides a direction towards settling the ongoing debate over the effect of Ce on the Mn active species. We postulate that the activity of the Mn active sites is not positively affected by Ce species in intimate contact. In fact, our results suggest that Ce is decreasing the average oxidation state and activity of Mn active species and is just a structural promotor, increasing catalyst surface area. On the other hand, addition of Ce is increasing N₂ selectivity as it

suppresses second step oxidation and thus N_2O formation by a dilution effect on the MnOx active sites. The latter still makes Ce an attractive additive for Mn-Ti systems.

Methods

Catalyst preparation. Titanium(IV) sulfate solution ($\text{Ti}(\text{SO}_4)_2$, Pfaltz & Bauer., 30 % in H_2SO_4), cerium(III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, 99.999% trace metals basis), manganese(II) nitrate hydrate ($\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, Sigma-Aldrich, 99.999% trace metals basis), ammonium hydroxide (NH_4OH , Alfa Aesar, ACS grade, 28.0-30.0%) were used as received, without further purification.

A series of individual, binary and ternary materials with different molar concentrations were prepared by a controlled co-precipitation method as described in the Supplementary information and Supplementary Fig. 1. Our method is a novel and highly efficient approach, where the aim is to precipitate all metals at the same pH level to obtain a homogeneously well-mixed metal oxide system. This is done by dual dosing of NH_3 and salt solution at a constant predetermined volumetric ratio. In most literature, the salt solution is added dropwise to an NH_3 solution, but this gives a pH change over time (from high to final low pH) and could lead to a suboptimal co-precipitation of the elements. First manganese nitrate hydrate ($\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$), and cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were dissolved in deionized water and stirred for 10 minutes. Then, a 30% titanium sulfate solution [$\text{Ti}(\text{SO}_4)_2$] in H_2SO_4 was added to the salt solution. These solutions were mixed under magnetic stirring at a constant speed (400 rpm) for 30 minutes, leading to a perfectly mixed metal salt solution. The mixed metal salt solution (loaded in a syringe pump) was injected simultaneously along with 14.7 M solution of ammonium hydroxide with a Gilson pump (NH_4OH , Sigma-Aldrich, 97%) to a recipient containing 20 ml of mother solution that is already at the target pH of 10.5. During this simultaneous injection of the metal precursor and base, the resulting suspension was continuously stirred. This procedure allows to operate at a constant pH of around 10.5 by adding the same amount of hydroxide consumed during the catalyst precipitation reaction. The metal oxides will precipitate at the same time,

rendering a very high level of homogeneity. Then, the precipitated solution was stirred for 30 min at 400 rpm. The sample was centrifuged at 7000 rpm and washed several times with milli-Q water until the conductivity of the supernatant reached to $50 \mu\text{s} \cdot \text{cm}^{-1}$. Then the samples were dried overnight at 100°C , followed by calcination at 500°C for 6 h. The list of samples and compositions is shown in Supplementary Table 1.

Catalyst characterization. X-ray diffraction patterns were obtained using a Bruker D8 Advanced A25 diffractometer in Bragg-Brentano geometry with $\text{Cu K}\alpha, \beta$ radiation source operated at 40 kV and 40 mA. β radiation is filtered out with a Ni plate. The diffractograms were measured with step size of 0.05° in the 2θ range of $10\text{--}80^\circ$. Nitrogen adsorption and desorption isotherms of the samples were measured at 77 K using Micromeritics ASAP-2420 surface area and porosity analyzer instrument. Samples were previously evacuated at 300°C for 3 hours. Specific surface areas and pore size distribution were calculated according to multi-point Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halenda (BJH) method, respectively. From the adsorption data, total pore volumes were estimated at $P/P_0 = 0.99$. The elemental compositions (Mn, Ce, Ti) of the samples were determined by an inductively coupled plasma spectrometer (Model 8900, Agilent Technologies). The samples were dissolved in HF and HCl. High-resolution Kratos Axis Ultra X-ray photoelectron spectroscopy equipped with a monochromatic Al $\text{K}\alpha$ source was used to determine the surface composition and chemical states of the samples. All analyses were monitored using the C 1s signal for adventitious carbon (284.8 eV). The chemical states of manganese in the catalysts were determined by peak modeling in CasaXPS software. To model the Mn $2p_{3/2}$ peaks of the catalysts, pure MnO , Mn_2O_3 and MnO_2 samples were used as reference. Manganese(IV) oxide (99.997% - metals basis) was acquired from Alfa Aesar (Fisher US), manganese(III) oxide (99.9% - trace metals basis) was acquired from Sigma Aldrich, and manganese(II) oxide (99.99% - trace metal basis) was acquired from Acros Organics (VWR). The fitting parameters data (FWHM and Peak positions) obtained from the peak modelling of the standard samples were used for the calculation of the chemical state of manganese in our catalysts. H_2 -TPR experiments were performed in Autochem 2950 instrument equipped with a thermal conductivity

detector. All catalysts (100 mg) were pretreated in a U-shaped quartz tubular micro-reactor in a flow of Ar at 250 °C for 2 h to yield a clean surface and then cooled down to 40 °C. Then, the temperature was raised from 40 to 1000 °C at a rate of 10 K/min under a flow of 10 vol. % H₂ (90 vol. % Ar). The acidity of samples was determined by temperature-programmed desorption of ammonia (NH₃-TPD). NH₃-TPD of samples was performed in a fixed bed quartz tube reactor. Prior to the measurement, the samples were first pretreated at 500 °C under N₂ flow. The reactor was cool down at 100 °C and samples were saturated with 1050 ppm NH₃ for 30 min. The samples were flush with N₂ for 30 min at room temperature, and then the temperature was increased to 500 °C at a rate of 10 K/min. The outlet gas composition (NH₃, NO, NO₂, N₂O) was monitored by using a MultiGas™ 2030 FTIR Continuous Gas Analyzer. High-resolution transmission electron microscopy (HRTEM) micrographs obtained from a Titan 60–300 TEM (FEI Co, Netherlands) equipped with an electron emission gun operating at 200 kV. The annular Dark-Field scanning transmission electron microscopy (ADF-STEM) in conjunction with electron energy loss spectroscopy (EELS) study was carried out with a Cs-Probe Corrected Titan microscope (Thermo-Fisher Scientific) which was also equipped with a GIF Quantum of model 966 from Gatan Inc. (Pleasanton, CA). STEM-EELS analysis was performed by operating the microscope at the accelerating voltage of 300 kV, using a convergence angle α of 17 mrad and a collection angle β of 38 mrad. Spectrum-imaging dataset includes the simultaneous acquisition of zero-loss and core-loss spectra (DualEELS) using a dispersion of 0.5 eV/channel and were recorded using a beam current of 0.2 nA and a dwell time of 50 ms/pixel. The Ti L_{2,3}-edge, Mn L_{2,3}-edge, and Ce M_{4,5}-edge were selected to build the chemical maps.

Catalyst testing. The catalytic activity measurements of the catalysts in the NH₃-SCR reaction were carried out in a fixed bed quartz tube reactor loaded with 0.5 ml of sample (PID Eng&Tech). Before loading, the catalysts were pressed into pellets, crushed and sieved to obtain a fraction between 500 and 710 μ m. The total flow was maintained at 1000 ml/min, and the reaction condition corresponds to GHSV of 120,000 hr⁻¹. The flow rate of gases was controlled using Bronkhorst mass flow controllers. A Controlled Evaporation and Mixing system (CEM) from Bronkhorst was used for evaporation of the

required H₂O in the gas feed before entering the reactor. The inlet gas stream contained 450 ppm NO, 500 ppm NH₃, 5 % O₂, 5 % H₂O and N₂ balance. A MultiGas™ 2030 FTIR Continuous Gas Analyzer was used to analyze the inlet and outlet gas compositions (NO, NO₂, NH₃, N₂O). The catalytic tests were performed in the temperature range of 150 – 500 °C (with an interval of 50 °C) at ambient pressure. The SCR activity (NO conversion) and N₂ selectivity are calculated as follows:

$$NO \text{ conversion } (\%) = \frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}} \times 100$$

$$N_2O \text{ selectivity } (\%) = \frac{2[N_2O]_{out}}{[NO_x]_{in} + [NH_3]_{in} - [NO_x]_{out} - [NH_3]_{out}} \times 100$$

Where [NH₃]_{in}, [NO_x]_{in}, [NH₃]_{out}, [NO_x]_{out}, and [N₂O]_{out} were the concentrations of NH₃ and NO_x(including NO and NO₂) at the inlet and those at the outlet.

Data Availability

The data supporting the findings of this article are available in the paper and in the Supplementary Information. Additional data are available from the corresponding author on reasonable request.

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Author contribution

L.E.G. and J.R.M. conceived, coordinated the research, designed the experiments and analyzed the data. L.R.E. and A.S. synthesized the catalyst materials and characterized them by TPD and BET. L.R.E. and A.S. performed the catalytic activity measurements. S.O.C. performed and analyzed the electron microscopy measurements. A.S. and M.N.H. performed and analyzed the XPS measurements. L.R.E., A.S. performed the XRD measurements and P.P.P. conducted the analysis. J.R.M. wrote the manuscript with the assistance of L.E.G., A.S. and L.R.E. All authors discussed the results and commented on the manuscript.

Competing interest

The authors declare no competing interest.

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