Stability Mechanism of Low Temperature C$_2$H$_4$−SCR with Activated-Carbon-Supported MnO$_x$-Based Catalyst

Fang Liu,* Jiangyuan Zhao, Shengbao He, Qing Liu, Guangli Liu, and Li Yang

ABSTRACT: Manganese-based catalysts have shown great potential for use as a hydrocarbon reductant for NO$_x$ reduction (HC-SCR) at low temperatures if their catalytic stability could be further maintained. The effect of CeO$_2$ as a promoter and catalyst stability agent for activated carbon supported MnO$_x$ was investigated during low temperature deNO$_x$ based on a C$_2$H$_4$ reductant. The modern characterization technology could provide a clear understanding of the activity observed during the deNO$_x$ tests. When reaction temperatures were greater than 180 °C and with ceria concentrations more than 5%, the overall NO conversion became stable near 70% during long duration testing. In situ DRIFTS shows that C$_2$H$_4$ is adsorbed on the Mn$_3$Ce$_3$/NAC catalysts to generate hydrocarbon activated intermediates, R-COOH, and the reaction mechanism followed the E-R mechanism. The stability and the analytical data pointed to the formation of stable oxygen vacancies within Ce$_3^+/Ce_4^+$ redox couplets that prevented the reduction of MnO$_2$ to crystalline Mn$_2$O$_3$ and promoted the chemisorption of oxygen on the surface of MnO$_x$-CeO$_x$ structures. Based on the data, a synergetic mechanism model of the deNO$_x$ activity is proposed for the MnO$_x$-CeO$_x$ catalysts.

1. INTRODUCTION

Large amounts of NO$_x$ emissions into the atmosphere lead to photochemical smog and chemical and eutrophication.$^1$−$^3$ Hence, NO$_x$ emission standards are becoming more rigorous, and NO$_x$ reduction technologies, such as NO$_x$ direct decomposition, selective noncatalytic reduction (SNCR), and selective catalytic reduction (SCR), have become more intensely investigated;$^4$−$^8$ of these, SCR is the most diffusely used technology to control NO$_x$ emission. The most established, commercial strategy for abating NO$_x$ emissions during SCR is to use NH$_3$ as the reductant,$^9$−$^{10}$ and commercial catalysts are based mainly on V$_2$O$_5$−WO$_3$/TiO$_2$.$^{11}$−$^{15}$ Ammonia is expensive; requires special handling, transport, storage, and application systems; and requires sophisticated metering to minimize NH$_3$ slip.$^{16,17}$ NH$_3$ slip causes plugging of ducts downstream of air-preheaters, forms secondary, fine particulate that is emitted into the atmosphere, and is regarded as an air pollutant potentially more objectionable than NO$_x$.$^{18,19}$ In addition, spent vanadium-based catalyst is classified as a detrimental solid waste, and its post processing is also costly.$^{18,19}$

In contrast with NH$_3$ hydrocarbons (HC) like C$_2$H$_4$ and C$_3$H$_8$ have low cost, high reducibility, user-friendliness, widespread distribution, and no NH$_3$ slip, and most importantly, they are byproducts in the refinery station,$^{20}$ so they can be directly used to reduce the NO$_x$ in the refinery station instead of long distance transportation and storage. Furthermore, hydrocarbons (HC) do not suffer from fouling by salt deposition, and some refinery stations have already used hydrocarbons (HC) to reduce NO$_x$. The overall Hydrocarbon-SCR reaction equation is as follows:

$$\text{C}_2\text{H}_4 + 2\text{NO} + (x + 0.25y - 1)\text{O}_2 \rightarrow \text{N}_2 + x\text{CO}_2 + 0.5y\text{H}_2\text{O}$$  (1)

In addition, vanadium-based NH$_3$−SCR operates in a narrow temperature window of 350−420 °C.$^{13}$ Hence, they are always used ahead of dust catcher and desulfurization systems to fulfill the desired temperature windows without extra heating. However, the presence of SO$_2$ and dust in these process locations reduces catalyst performance and durability.$^{21,22}$ Nevertheless, if the running temperature could be reduced to, for instance, less than 250 °C, then de-NO$_x$ facilities could be installed downstream of heat recovery steam generators (HRSG). Importantly, small-scale industrial boilers, such as steel furnaces, glass kilns, and coke ovens,
operate with flue gas temperatures about 200−300 °C and temperatures of desulfurization units below 200 °C. Under these conditions, vanadium-based catalysts would not be effective. Thereby, developing effective and stable catalysts using low-temperature (<200 °C) HC-SCR has become a scientific and development quest with important practical implications.

Among various catalyst active components investigated for HC-SCR of NOₓ, noble metals have shown promising results; for example, an Ag−Mg−Al composition (Ag-MgAl) at 350 °C exhibited 98% NO conversion. In general, however, noble metals have high costs, limiting their application in large-scale commercial operations; they are also not applicable for low-temperature HC-SCR reactions because their reactivities require temperatures near or higher than 350 °C. With concerns of low-temperature operating conditions, transition metal oxides served as potential candidates for HC-SCR catalysis because of their activity, low cost, and environmental acceptability. For example, NO conversion was reported while using Cu/ZSM-5 with C₃H₆ as a reductant; MnOₓ is known for its initial, high reactivity at low temperatures for HC-SCR reactions. Supports, such as Al₂O₃, TiO₂, SiO₂, and activated carbon (AC), have been used with MnO₂-based catalysts. Both SiO₂ and TiO₂ have demonstrated thermostability and acceptable mechanical capacities, while AC presents high surface area and porosity that imply the possibility of readily dispersing the active metal oxide and enabling reactant access to the active sites; however, most of these studies have used NH₃ as the reductant.

MnOₓ/AC was used with C₂H₄ as a reductant and exhibited over 90% NO conversion even at temperatures as low as 130 °C; it deactivated rapidly such that only 20% conversion was evident after only 2 h of testing. This deactivation was attributed to a combination of the following: first, the valence state of the Mn decreased from Mn⁴⁺ to Mn³⁺ and Mn²⁺, but Mn⁴⁺ was found to be more active than the other two valences; second, carbon black was deposited on the active carbon surface during SCR reaction testing, blocking channels, and active catalytic sites. Cerium oxides (CeO₂) have a specific fluorite structure, in which with each Ce⁴⁺ is surrounded by eight equivalent, nearest O²⁻ ions which formed the corners of a cube structure and coordinated to four Ce⁴⁺ ions. The ion configuration contributes to a high oxygen storage capacity, a vast number of oxygen vacancies, and strong redox properties between Ce³⁺ and Ce⁴⁺, which may help maintain the stability of MnO₂. Therefore, ceria as an additive was considered a strong candidate to help promote and maintain the catalytic performance of MnO₂-based catalysts during HC-SCR reaction testing at low temperatures.

Characterization data shows that there were a number of oxygen defects produced by Mn³⁺ + Ti⁴⁺ ↔ Mn⁴⁺ + Ti³⁺ and...
Ce⁴⁺ + Mn³⁺ ↔ Ce³⁺ + Mn⁴⁺, which was a beneficial improvement of deNOₓ, these two reactions generated a charge imbalance, oxygen vacancies, and unsaturated chemical bonds on the catalyst surface.⁴⁵,⁴⁶

This study will investigate the catalytic performance of ceria modified Mn/AC catalysts, and further explore the promotion mechanism of CeO₂, which could help develop stable and highly active HC-SCR catalysts. The effect of CeO₂ as a promoter and a catalyst stability agent for activated carbon supported MnOₓ will be investigated during low temperature deNOₓ based on C₂H₄ reductant. The modern characterization technology could provide a clear understanding of the activity observed during the deNOₓ tests.

2. RESULTS AND DISCUSSION

2.1. Dispersion of Active Component. SEM images and EDS elemental mappings of fresh Mn₃Ce₃/NAC catalyst are presented in Figure 1. The catalyst morphology was similar to that in previous studies,⁴⁷ the active components are evenly loaded on the surface of the activated carbon with particle structure. Elemental distributions indicated well-dispersed manganese and cerium on the NAC surface and without agglomeration,⁴⁷ which helps to improve the catalytic efficiency of the catalyst.

2.2. Catalytic Performance. Figure 2a shows the HC-SCR catalytic performance of Mn₃Ce₃/NAC at 150, 180, and 200 °C. Similar to MnOₓ/NAC without CeO₂, excellent NO conversion was observed at 150 and 180 °C during the first 20 min of testing, but large decreases in NO conversion then occurred, such that only about 20% NO conversion remained after 2 h of reaction testing. In contrast, at 200 °C after an initial sharp drop in conversion, the activity was constant at 65% over the entire 2 h period of testing. This may be because at the initial stage of the reaction, most of Mn and Ce in the fresh catalyst are in the forward direction in the catalytic reduction reaction, but the reaction is not balanced at this time. After the chemical reaction is in equilibrium, the NO conversion rate tends to be stable, and the valence state

![Figure 2. (a) NO conversion. (b) N₂ selectivity of Mn₃Ce₃/NAC using C₂H₄ as a reductant. Reaction temperature varied from 150 to 200 °C; reaction conditions were 500 ppm of NO, 250 ppm of C₂H₄, and 3% O₂ with a flow rate of 1500 mL/min.](image)

![Figure 3. (a) NO conversion and (b) N₂ selectivity of Mn₃Ceₓ/NAC (x = 3, 5, 7) used C₂H₄ as a reductant. Reaction temperature was 180 °C, and the reaction conditions were 500 ppm of NO, 250 ppm of C₂H₄, and 3% O₂ with a flow rate of 1500 mL/min.](image)
changes of Mn and Ce in the catalyst also tend to be stable. N₂O less than 2 ppm was measured by GC, so it was not discussed in this study. The N₂ selectivity of Mn₃Ce₃/NAC is shown in Figure 2b; it could remain at a high level for above 90%, especially for reaction at 200 °C, where the N₂ selectivity reached 100% during overall reaction time.

Effects of the Ce loading on NO conversion and N₂ selectivity at 180 °C were investigated (Figure 3). The NO conversion times for Mn₃Ce₃/NAC and Mn₃Ce₅/NAC were very similar to the results from MnCe/NAC as shown in Figure 2a when the reaction temperatures were either 150 or 180 °C. However, when the Ce loading was increased to 7% and the reaction temperature was 180 °C, the NO conversion rate remained stable over the entire period of the testing. By comparing the data in Figure 2a and Figure 3a, it was concluded that both reaction temperatures and CeO₂ concentrations can affect NO conversion rates and stabilities during HC-SCR.

The presence of CeO₂ has been shown to be capable of mitigating the deactivation of Mnₓ/NAC catalysts during low temperature HC-SCR reaction testing. Hence, physical and chemical differences in MnCe/NAC catalysts were investigated before and after reaction testing to shed light on changes which may affect NO conversion rates.

2.3. Promoting Mechanism of Ce Loading. 2.3.1. Effect of Ce Addition on the Surface Area. As displayed in Table 1, the BET surface areas were decreased by about 15% upon impregnating CeO₂ onto a MnO₂/NAC catalyst, but its surface area was not significantly different after reaction testing; these results suggest that MnO₂ and CeO₂ had minimal influence on the textural properties and the surface structure of the catalyst. Although the larger surface area is known to be beneficial to the chemical reactivity of HC-SCR reactions, it was not the key to affecting the catalytic activity of Mn₃Ce₃/NAC, because the decrease of catalytic performance was more drastic than the change of surface area.

2.3.2. Morphology Evolution. The SEM/EDS images in Figure 4 and Figure 5, respectively, display morphologies and sizes of the Ce-rich and Mn-rich particles of Mn₃Ce₃/NAC after HC-SCR reaction testing at 150 and 200 °C. During the experiment, the state of the activated carbon support did not change significantly before and after the reaction. As compared to the as-prepared catalyst, reaction testing caused growth in the sizes of both Mn- and Ce-rich particles, but the EDS data also suggest that the Mn was more highly dispersed after 200 °C testing than after 150 °C testing. This difference may be related to an increased probability of interactions between Ce and Mn which enabled continued, stable NO conversion at 200 °C as opposed to the steady decrease in NO conversion at 150 °C.

2.3.3. Crystalline Phases. The XRD patterns of Mn₃Ce₃/NAC tested at 200 °C were very similar before and after reaction testing, whereas the XRD pattern of the catalyst tested at 150 °C was different, the intensity of XRD peaks for the sample after the reaction at 150 °C decreased. Interpreting the exact contributions to peak intensities from the various compounds was complicated, because it required deconvolution of overlapping peaks due to amorphous carbon, CeO₂, MnO₂ and Mn₃O₄. However, if the intensity contributions from amorphous carbon to the peak at 2θ = 24° and 2θ = 43° were approximately constant—indicated by the fact that the peak intensity from carbon at 2θ = 43° was mostly unchanged independent of whether the fresh catalysts tested at 150 or 200 °C were examined—then the overall intensity changes in the 2θ = 20–30° composite peak were primarily caused by differences in concentrations and/or crystallinities of the metal oxides. In addition, the intensity of the CeO₂ peak at 79.1° was slightly less in the fresh than in catalyst tested at 200 °C, indicating different crystallinity for CeO₂ in the catalyst tested at 150 °C; as a consequence, it would contribute to distinct shoulders in peak intensities at 28.5°, 47.5°, and 56.3°. Simultaneously, the peak at 56.3° was most pronounced in the catalysts tested at 200 °C, thereby implying that the concentration and/or crystallinity of MnO₂ was distinct in the catalysts tested at 200 °C as compared to the other tested catalysts. Therefore, the MnO₂ and CeO₂ components of the catalysts tested at 200 °C were more stable than those tested at 150 °C. The stability in the crystalline

Table 1. Specific Surface Area

| samples                             | BET surface area (m²/g) |
|-------------------------------------|-------------------------|
| Fresh AC                            | 439.07                  |
| Mnₓ/NAC Before Reaction             | 668.54                  |
| Mn₃Ce₅/NAC Before Reaction          | 599.35                  |
| Mn₃Ce₃/NAC After 150 °C Reaction    | 547.72                  |
| Mn₃Ce₃/NAC After 200 °C Reaction    | 571.40                  |

Figure 4. Morphology of Mn₃Ce₃/NAC after reaction testing of 150 °C. (a) SEM image Mn₃Ce₃/NAC, 2000x. (b) EDS image of Mn/Ce element dispersion.
phase may enable the catalysts tested at 200 °C to maintain the oxidation state of Mn and its catalytic performance.

2.3.4. H2-TPR Analysis. The H2-TPR data shown in Figure 7 exhibited a TPR profile that was deconvoluted into three distinct peaks between 200 and 800 °C. Reduction of the weakest Mn−O bonds occurred at the temperature region $T_1$ and was for MnO$_2$ to Mn$_2$O$_3$; the amorphous Mn$_2$O$_3$ was then reduced to Mn$_3$O$_4$ before converting to MnO at temperature $T_2$. The reduction of CeO$_2$ was mainly concentrated between 518 and 787 °C and assigned to the $T_3$ temperature. Before reaction testing, the two main reduction peaks were at 442 and 644 °C, in which the 442 °C peak was attributed to Mn$_2$O$_3$ and the peak at 644 °C was assigned to surface reduction of CeO$_2$; the 442 °C peak could accounted for reduction of surface Ce$^{4+}$ to Ce$^{3+}$. For the 150 °C reaction tested sample, the intensity of the 442 °C peak was greater than before testing, indicating more Mn$_2$O$_3$ after testing. From the literature, it is expected that the reduction of MnO$_x$ to MnO would involve the presence of Mn$_3$O$_4$. However, after 200 °C reaction testing, the higher peak intensity at 644 °C pointed to relatively high concentrations of Ce$^{4+}$; also, for this sample, the broad, high-intensity reduction peak near 518 °C was due to the reduction of surface oxygen of ceria.

2.3.5. C$_2$H$_4$-TPD/NO-TPD Analysis. The C$_2$H$_4$-TPD and NO-TPD data were shown in Figure 8. At 80−700 °C, Mn$_3$Ce$_3$/NAC catalysts had 3 desorption peaks for C$_2$H$_4$ and NO. In C$_2$H$_4$-TPD, the desorption peaks of the Mn$_3$Ce$_3$/NAC catalysts: (a) before reaction; (b) after 150 °C reaction; (c) after 200 °C reaction.

Figure 5. Morphology of Mn$_3$Ce$_3$/NAC after reaction testing of 200 °C. (a) SEM image Mn$_3$Ce$_3$/NAC, 2003X. (b) EDS image of Mn/Ge element dispersion.

Figure 6. XRD pattern of Mn$_3$Ce$_3$/NAC catalyst: (a) before reaction testing; (b) after 150 °C reaction testing; (c) after 200 °C reaction testing.

Figure 7. H$_2$-TPR profiles of Mn$_3$Ce$_3$/NAC catalysts: (a) before reaction; (b) after 150 °C reaction; (c) after 200 °C reaction.

Figure 8. C$_2$H$_4$-TPD and NO-TPD of Mn$_3$Ce$_3$/NAC catalysts.
catalyst were located at 156, 373, and 591 °C. The 156 °C peak corresponded to the medium-strong acid site, and the peaks at 373 and 591 °C were attributed to the strong acid site. It can be seen from the C2H4-TPD spectrum that the distribution of medium-strong acid centers was greater than that of strong acid. The NO-TPD spectrum shows that the desorption peaks of the Mn3Ce3/NAC catalyst were distributed at 160, 316, and 396 °C. At 160 °C, the NO desorption peak was very small; that is, the corresponding medium-strong acid site content was relatively low, which indicated that under low temperature conditions, C2H4 was more easily adsorbed on the surface of Mn3Ce3/NAC catalyst.

2.3.6. In Situ DRIFTS Study. Figure 9a shows the DRIFTS spectra of Mn3Ce3/NAC catalysts in a flow of NO + O2 + He at 200 °C. When the mixed gas was introduced for 1 min, a strong band appeared at 2350 cm⁻¹, which was attributed to CO2.56 Over time, other bands at 1910, 1850, 1630, 1590, 1310, and 844 cm⁻¹ were detected. The peak at 1910 cm⁻¹ corresponded to C−H; 1850 cm⁻¹ peak was assigned to acid anhydride; 1630, 1590, and 1310 cm⁻¹ were the characterization signals of NO2−;57 and the band at 844 cm⁻¹ was attributed to νasC−N. Therefore, nitrates on Mn3Ce3/NAC catalyst were formed from the reaction between NO and O2.

Figure 9b shows the DRIFTS spectra of Mn3Ce3/NAC catalysts in a flow of C2H4 + O2 + He at 200 °C. After the mixed gas was introduced, two strong absorption peaks appeared at 2350 and 2980 cm⁻¹, respectively; the peak at 2350 cm⁻¹ was consistent with the band in Figure 10, which corresponds to CO2, while the peak at 2980 cm⁻¹ was attributed to the CH2 and CH3 stretching vibrations.58

Figure 9c shows the DRIFTS spectra of Mn3Ce3/NAC catalysts in a flow of C2H4 + NO + O2 + He at 200 °C. At time of 1 min, there were 5 bands, and they were located at 2980, 2350, 984, 949, and 910 cm⁻¹, respectively. Among them, the peak at 2980 cm⁻¹ was assigned to CH2 and CH3 stretching vibrations,58 the band at 949 cm⁻¹ was attributed to νasO−H of R-COOH, the band at 2350 cm⁻¹ was attributed to CO2, the peak at 984 cm⁻¹ was attributed σC−H of olefin, and the band at 910 cm⁻¹ belongs to C−N. The band intensity at 1524 cm⁻¹ was weak, and it belonged to νasCOO−.56

Comparing Figure 9a–c, there was an absorption CO2 peak under the three gas flow conditions, which may be the result of the oxygen-containing functional groups in the activated
carbon being oxidized by oxygen. From Figure 9a, it can be inferred that after the introduction of NO and O₂, NO was adsorbed on the surface of the Mn₃Ce₃/NAC in situ catalyst and generated nitrate. Figure 9b shows that ethylene had a good adsorption capacity on the Mn₃Ce₃/NAC catalyst and produced the important intermediate products in the HC-SCR, which can be partially oxidized to generate hydrocarbon activated intermediates. Figure 9c demonstrated that when C₂H₄ + NO + O₂ was introduced, strong peaks R-COOH and weak peak of unidentate nitrate appeared, which indicated that ethylene was more easily adsorbed on the catalyst surface.

Based on the above results, during the HC-SCR reaction, the C₂H₄⁻SCR reaction route was determined as the ethylene being first adsorbed on Mn₃Ce₃/NAC catalysts to produce the intermediate products containing CH₂ or CH₃, and then reacted with NO to further produce products containing R-COOH, nitro, and C-N, and finally decomposed into final products H₂O, CO₂, and N₂, which indicated that the C₂H₄⁻SCR reaction following the E-R mechanism.⁵⁹⁻⁶¹

2.3.7. Binding State of Constituent Elements. Oxidation states of catalytically active species worked as an essential role in the catalytic performance,⁶² hence, XPS analyses of the Mn₃Ce₃/NAC catalysts were also performed, the data from which are presented in Figures 10, 11, and 12. As shown in Figure 10, the main peaks of Mn 2p deconvoluted into contributions from respective oxidation states, including 642.4, 641.2, and 640.5 eV corresponding to Mn⁴⁺, Mn³⁺, and Mn²⁺, respectively.⁶³ Similarly, the peaks at 654.1, 652.8, and 651.1 eV were ascribed to Mn⁴⁺, Mn³⁺, and Mn²⁺ for Mn 2p½, respectively.⁶³ In addition to contributions to peak intensities from the three oxidation states of Mn, the intensity ratios of Mn⁴⁺/(Mn³⁺ + Mn²⁺ + Mn⁴⁺) and Mn²⁺/(Mn²⁺ + Mn³⁺ + Mn⁴⁺)—labeled as Mn⁴⁺/Mnᵣ and Mn²⁺/Mnᵣ ratios in Table 2—are presented in Table 2. The catalyst before and after it was tested at 200 °C had high Mn⁴⁺/Mnᵣ ratios near 41%, whereas this ratio was 30% after 150 °C reaction testing. Hence, the contribution of Mn⁴⁺ was significantly less in the catalyst tested at 150 °C; it matched the XRD results in which the intensity of peaks for the catalyst after the reaction at 150 °C decreased.

Relative to the contribution of Mn⁴⁺ to HC-SCR, it is known that the activity of MnO₂ species follows the order of MnO₂³ < Mn₃O₈ < Mn₃O₇ < Mn₃O₄ < MnO,⁶⁴ suggesting that the existence of high oxidation state Mn was favorable for NO conversion. Furthermore, the acceleration effect of Mn⁴⁺ to the oxidation of NO to NO₂ has been attested, which could then impact SCR reactions through a “fast SCR” pathway.⁶⁵ Less Mn⁴⁺ in the catalyst tested at 150 °C was also suggested by the H₂-TPR data.

As shown in Figure 11, the Ce 3d spectra of the fresh and tested catalyst samples were split into nine main peaks. There are four pairs of spin–orbit doublets, and the nine peaks at 882.3, 884.6, 885.8, 888.5, 898.3, 900.8, 904.9, 907.3, and 916.7 eV were respectively marked as O₂ −, O₂ −, O₂ −, O₂ −, O₂ −, O₂ −, O₂ −, O₂ −, O₂ −. Relative to the contribution of Mn⁴⁺ to HC-SCR, it is known that the activity of MnO₂ species follows the order of MnO₂³ < Mn₃O₈ < Mn₃O₇ < Mn₃O₄ < MnO,⁶⁴ suggesting that the existence of high oxidation state Mn was favorable for NO conversion. Furthermore, the acceleration effect of Mn⁴⁺ to the oxidation of NO to NO₂ has been attested, which could then impact SCR reactions through a “fast SCR” pathway.⁶⁵ Less Mn⁴⁺ in the catalyst tested at 150 °C was also suggested by the H₂-TPR data.

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and U”. Due to the spin–orbit of the Ce 3dₓ/₂ and Ce 3dᵧ/₂, the peaks were labeled V and U, respectively.⁶⁶⁻⁶⁷ The V₋ V, V₋ U, U₋ U”, and U₋ U” peaks were associated with the Ce⁴⁺, while the peaks denoted as U₋′ U”, and V’ corresponded to the Ce⁴⁺ species. Hence, the coexistence of Ce⁴⁺ and Ce⁴⁺ in Mn₃Ce₃/NAC was confirmed through the Ce 3d XPS spectra. It was discovered that the coexisting ion pair Ce⁴⁺/Ce⁴⁺ species could create a charge imbalance, unsaturated chemical bonds, and oxygen vacancies on surfaces; these were in favor of the formation of chemisorbed oxygen during reaction testing.⁶⁸

As shown in Table 2, the ratio of [Ce⁴⁺/(Ce⁴⁺ + Ce⁴⁺)] in the fresh catalyst and after 200 °C reaction testing was about 80%. According to the literature,⁶⁹ the incorporation of Ce in Mn compounds can create a Mn–O–Ce bridge during CeO₂ formation which also strengthens the bond between Mn and oxygen and promotes the valence of Mn from Mn³⁺ to Mn⁴⁺ through Mn₃O₃ + 2CeO₂ → 2MnO₂ + Ce₂O₃. Hence, the existence of an oxygen vacancy and facile Ce³⁺/Ce⁴⁺ couple could prevent the reduction of MnO₂ to Mn₂O₃ while simultaneously creating larger Ce⁴⁺ concentrations through the redox cycle of Mn³⁺ + Ce⁴⁺ ↔ Mn⁴⁺ + Ce³⁺.⁷⁰ Then, the presence of a stable Mn⁴⁺ is suggested to facilitate HC-SCR reactions. In other words, the 79% and 81% Ce⁴⁺ ratios on the fresh and 200 °C reaction tested samples, and the stable NO conversion, are in accordance with this interpretation.

Figure 12 describes the XPS spectra for O 1 s of the catalysts in which the deconvolution of the peaks was accomplished using three peaks. The binding energies of peaks were in which the deconvolution of the peaks was accomplished with the Ce⁴⁺, while the peaks denoted as U₋′ U”, and V’ corresponded to the Ce⁴⁺ species. Hence, the coexistence of Ce⁴⁺ and Ce⁴⁺ in Mn₃Ce₃/NAC was confirmed through the Ce 3d XPS spectra. It was discovered that the coexisting ion pair Ce³⁺/Ce⁴⁺ species could create a charge imbalance, unsaturated chemical bonds, and oxygen vacancies on surfaces; these were in favor of the formation of chemisorbed oxygen during reaction testing.

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Figure 12 describes the XPS spectra for O 1 s of the catalysts in which the deconvolution of the peaks was accomplished using three peaks. The binding energies of peaks were approximately 529.6, 531.1, and 533.2 eV, credited to lattice oxygen (O⁺, marked as Oₐ), surface chemical oxygen (O₂⁻ or O⁺, marked as Oₐ), and the oxygen species in hydroxide groups which was marked as Oₓ, respectively.⁷¹ The relative intensity of Oₓ changed intensely after the HC-SCR reactions. Thus, the surface chemisorbed oxygen has also been more correlated to higher catalytic activity than lattice oxygen as a result of its higher mobility.⁷² As shown in Table 2, the ratios of Oₓ changed intensely after the HC-SCR reactions. Therefore, the analytical characterization data of Mn₃Ce₃/NAC catalysts before and after the reaction testing point to a reaction sequence during HC-SCR as depicted in Figure 13. The presence of CeO₂ in a sufficient concentration is critical for stable NO conversion, because it helps to prevent the reduction of MnO₂ to Mn₂O₃ by promoting the forward reaction and simultaneously, through synergistic interactions, promotes the establishment of relatively high concentrations of facile, absorbed oxygen on the catalyst surface. Therefore, C₂H₄ is more easily oxidized to produce the hydrocarbon activated intermediate, –COOH, which promotes the C₂H₄–SCR reaction. When the CeO₂ concentrations were not high enough or the reaction temperature was too low, a precipitous decrease in NO activity occurred immediately after reaction testing had begun, because the Ce species were agglomerated into small, isolated CeO₂ crystallites which did not effectively interact with the MnO₂ and did not mitigate the formation of low-activity Mn₃O₄ species.

3. EXPERIMENTAL METHODS

3.1. Catalyst Preparation. Active carbon was purchased from MACKLIN with particle size range of 1000–2350 μm. The raw AC was first treated with 10% HNO₃ solution for 4 h under room temperature and washed with deionized water until the pH of the wastewater became neutral, and finally the AC was dried under air atmosphere at 140 °C for 14 h. These HNO₃-treated AC supports were named as NAC.

The Mn–Ce/AC catalysts with MnO₂ and CeO₂ loadings were prepared by impregnation of the NAC using Mn(NO₃)₂·4H₂O and Ce(NO₃)₃·6H₂O solutions to attain a Mn loading of about 3.0 wt % and Ce loadings of 3.0, 5.0, and 7.0 wt %; sonication of these mixtures was at room temperature for 2 h. Then, the hybrids stand for 12 h, after which they were filtered and dried in a vacuum oven heated to 110 °C, and finally calcined at 400 °C for 2 h in a hermetic muffle furnace under N₂ atmosphere. The synthesized materials were labeled as Mn₃Ce₃/NAC, where X = 3, 5, 7.

3.2. Catalyst Characterization. The synthesized materials were characterized analytically before and after reaction testing. After degassing overnight at 160 °C and isothermal N₂ adsorption–desorption measurements taken at 77 K, surface area and porosity were measured in a Micromeritics ASAP 2020 analyzer.

Crystalline structures were performed by X-ray diffraction (XRD) using Cu Kα irradiation with a 2θ range of 90°. The microstructure was examined by scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher ESCALAB 250Xi instrument, and the data were calibrated using the ubiquitous Cls peak at 284.8 eV.

The temperature-programmed reduction (TPR) data were acquired using an AutoChem II 2920 instrument; approximately 0.1 g samples were placed in a U-shaped quartz tube which was then pretreated in O₂ flow at 300 °C for 1 h. After the samples were cooled to room temperature, 5% H₂ in helium was flowed through the tube at a flow rate of 30 mL/min while the temperature was increased from room temperature to 900 °C at a rate of 10 °C/min.

The temperature-programmed desorption (TPD) study was performed on an AutoChem II 2920 instrument: 0.1 g sample was pretreated in helium at 300 °C for 1 h; afterward the sample was cooled to room temperature, and C₂H₄ or NO in helium was purged to the tube at a flow rate of 30 mL/min as the temperature was increased from 80 to 700 °C at a rate of 10 °C/min.

Figure 13. Synergistic mechanism for HC-SCR of NO on Mn₃Ce₃/NAC catalysts.
In situ DRIFTS was performed on a VERTEX 80 V instrument: 0.2 g sample was pretreated in helium at 200 °C for 30 min, and signals were collected as the background spectrum. Then, the NO + O₂, C₂H₄ + O₂, and C₂H₄ + NO + O₂ was separately flowed into the reactor at 30 mL/min, and the sample spectra at 1, 3, 5, 10, 15, 20, 25, and 30 min were collected (scanning times, 128; resolution, 4 cm⁻¹; scanning range, 4000–600 cm⁻¹).

3.3. Catalytic Activity Testing. The activity evaluation equipment of the prepared catalysts (Figure 14) involved a fixed bed, a gas analyzer (MRU MGAS), a gas cleaning unit, several mass flow controllers (MFCs, MF SHY 400), and a quartz tube reactor (I.D. = 10 mm) heated by a temperature-controlled furnace; the initial weight of a sample for each test was 10 g. Total gas flow at a rate of 1500 mL/min was controlled by mass flow controllers (MFCs, MF SHY 400). The components of the simulated flue gas were 500 ppm of NO, 250 ppm of C₂H₄, 3 vol % O₂, and N₂ as a balance. The catalyst sample was in N₂ atmosphere during the heating procedure; once the temperature remained unchanged, the mixture was flowed into the reactor, and then NO and NO₂ gas concentrations at the outlet of the reactor were analyzed using a flue gas analyzer (MRU). From these concentration data, NO conversion and N₂ selectivity data were calculated through the following equation:

\[
\text{NO conversion(\%)} = \left(1 - \frac{[\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}}\right) \times 100 \tag{2}
\]

\[
\text{N₂ selectivity(\%)} = \left(1 - \frac{[\text{NO}]_{\text{out}} + 2 \times [\text{N₂O}]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}\right) \times 100 \tag{3}
\]

4. CONCLUSIONS

This study focused on examining the potential development of stable and active MnₓCeₓ/NAC catalysts used for HC-SCR with C₂H₄ as a reductant and on understanding catalyst physical and chemical properties important for NO conversion with temperatures at or below 200 °C. The catalysts were prepared, tested for HC-SCR catalytic activity, and analyzed before and after reaction testing using surface sensitive and bulk techniques. The conclusions include the following:

1. The addition of CeO₂ to the MnOₓ established stable and high HC-SCR catalytic performance when the reaction temperature was at least 200 °C and the CeO₂/MnOₓ concentration ratio was 1 or reaction temperature was below 200 °C and the CeO₂/MnOₓ concentration ratio was > 1.

2. The reaction mechanism followed the E-R mechanism, and ethylene was first adsorbed on the MnₓCeₓ/NAC catalysts to produce the intermediate products containing CH₂ or CH₃, which can be partially oxidized to generate hydrocarbon activated intermediate, R-COOH.

3. Stable activity was proposed to be a result of the formation of CeO₂ at a sufficient concentration that could prevent the reduction of Mn⁴⁺ and, simultaneously, the creation of Ce³⁺/Ce⁴⁺ redox couples that would help to reoxidize any reduced Mn.

4. The addition of CeO₂ promoted the formation of Mn–O–Ce bridges with MnOₓ that then helped to enhance the concentration of surface chemisorbed oxygen and oxygen vacancies. This study provided new and intriguing insight into approaches to instill effective catalytic activity into transition metal oxide catalysts for low-temperature HC-SCR applications.

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Notes
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