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Low Temperature deNO_x Catalytic Activity with C₂H₄ as a Reductant Using Mixed Metal Fe-Mn Oxides Supported on Activated Carbon

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Abstract: The selective catalytic reduction of NO_x (deNO_x) at temperatures less than or at 200 °C was investigated while using C₂H₄ as the reductant and mixed oxides of Fe and Mn supported on activated carbon; their activity was compared to that of MnO_x and FeO_x separately supported on activated carbon. The bimetallic oxide compositions maintained high NO conversion of greater than 80–98% for periods that were three times greater than those of the supported monometallic oxides. To examine potential reasons for the significant increases in activity maintenance, and subsequent deactivation, the catalysts were examined by using bulk and surface sensitive analytical techniques before and after catalyst testing. No significant changes in Brunauer-Emmett-Teller (BET) surface areas or porosities were observed between freshly-prepared and tested catalysts whereas segregation of FeO_x and MnO_x species was readily observed in the mono-oxide catalysts after reaction testing that was not detected in the mixed oxide catalysts. Furthermore, x-ray diffraction and Raman spectroscopy data detected cubic Fe₃Mn₃O₈ in both the freshly-prepared and reaction-tested mixed oxide catalysts that were more crystalline after testing. The presence of this compound, which is known to stabilize multivalent Fe species and to enhance oxygen transfer reactions, may be the reason for the high and relatively stable NO conversion activity, and its increased crystallinity during longer-term testing may also decrease surface availability of the active sites responsible for NO conversion. These results point to a potential of further enhancing catalyst stability and activity for low temperature deNO_x that is applicable to advanced SCR processing with lower costs and less deleterious side effects to processing equipment.

Keywords: synergistic effects; transition-metal oxides; deactivation; selective catalytic reduction; catalytic activity enhancement

1. Introduction

Nitrogen oxides (NO_x) are created during fossil fuel combustion and participate in the formation of acid rain and photochemical smog [1–4]. Consequently, deNO_x technologies have been widely studied and commercially-practiced throughout the world [5]; these include NO_x direct decomposition, selective catalytic reduction (SCR), and selective non-catalytic reduction (SNCR) [6]. Among the most successful and applied deNO_x technologies is SCR of NO_x using ammonia (NH₃) as the reductant (NH₃-SCR).

The most widely used NH₃-SCR catalyst in stationary power plants and refineries is V₂O₅/WO₃/TiO₂ [7–11]. Despite its high activity and stability during deNO_x reactions, the need

to maintain temperatures in a range of 300–420 °C requires additional external heating if the catalyst is located downstream of particulate collectors [12] and desulfurization units [13] where temperatures are normally below 200 °C. If located upstream of particulate collection and desulfurization units, the temperatures are compatible with those needed for V₂O₅/WO₃/TiO₂ catalysts but significant particulate accumulation on the catalyst and sulfur poisoning will cause rapid deactivation [12–14]. Additionally, in this higher-temperature location, the presence of the NH₃ reductant causes the formation of ammonium salts (ammonium sulfate or ammonium bisulfate) [15] which crystallize and deposit [16] on downstream flow pipes of waste heat boilers; this deposition causes fouling and blockages that endanger the long-term operation of catalytic systems [17]. The stability and durability are critical in commercial catalyst application and the life time of current employed NH₃-SCR catalyst is about 16,000 h. Ammonia is also a poisonous gas at concentrations higher than 500 mg/m³, and strict precautions are required for safety during transportation, storage and use [17,18]. Furthermore, spent vanadium-based catalysts are considered hazardous wastes, and require specialized post-treatment that is difficult and costly [19].

To overcome the issues and difficulties associated with V₂O₅/WO₃/TiO₂ deNO_x technology, it would be beneficial if operating temperatures of deNO_x catalysts could be lowered to less than 250 °C. If successful, they could be installed downstream of a heat recovery steam generator (HRSG) unit to avoid deposition and the resulting blockage of heat exchangers. Interestingly, the temperature ranges of the flue gases from a majority of small-scale industrial boilers like coke ovens, steel furnaces, and glass kilns already fall within 200–300 °C and can be even lower than 200 °C after desulphurization units in these boilers [20]. Currently-used vanadium-based catalysts would be inefficient at these temperatures [8]. Therefore, significant impetus exists to develop alternative SCR deNO_x catalysts having high and stable performance at lower temperatures than now commercially practiced. For example, Zhu et al. [21] developed an excellent low temperature NH₃-SCR catalyst based on Mn_aCe_{0.3}TiO_x (a = 0.1–0.3) oxides, and reported a 100% NO conversion and above 90% N₂ selectivity between 175 °C and 400 °C; Shih et al. [22] found that a Mn and Ti-containing catalyst provided a NO reduction rate of 83% at a relatively low temperature of 200 °C. Other methods such as the use of plasma could also enhance catalytic conversion of NO at low temperatures [23,24].

Hydrocarbons, such as C₂H₄, have been examined as a replacement reductive in place of NH₃ during deNO_x reactions under lean conditions (labeled as HC-SCR). The overall reaction equation of HC-SCR can be written as:

HC-SCR is promising for the removal of NO_x under lean conditions since this method exploits unburned hydrocarbons already present in the exhaust gas stream [25]. However, there are some drawbacks along with hydrocarbons such as the increase in CO₂ emissions, the cost of reducing agent and hydrocarbons are also air pollutants. However, the CO₂ formed by C₂H₄ is very minor compared with the coal combustion and can be neglected.

Current developed HC-SCR catalysts with excellent catalytic performance are mainly two types: Noble metal oxides and metal-exchanged zeolites. Xu et al. [26] found Ag/Al₂O₃ exhibited almost 100% in the temperature region of 300–500 °C during H₂-C₃H₆-SCR. However, as we have discussed before, the existence of SO₂ in the flue gas will cause the catalyst deactivated quickly and NO_x conversion stabilized at 25%. The SCR catalyst used in power plants have strict requirement of its life to insure long-term operation. The stability and cost shortcoming of noble metal catalyst caused all the studies remained at laboratory conditions. Metal-exchanged zeolites also present good NO_x conversion value in high temperature region (300–500 °C), but Valerie Houel et al. [27] showed that Cu/ZSM-5 catalyst was fairly insensitive to SO₂ compared with Ag/Al₂O₃. Therefore, the HC-SCR catalysts are far away from commercial application due to the stability and durability requirement in power plant and other small-scale industrial boilers.

Non-vanadium catalysts have been examined in HC-SCR reaction testing and may provide an approach for circumventing the problems of current NH_3 -SCR technologies [17]. The basis of these catalysts include transition metal oxides containing manganese, iron or copper [28,29], supported noble metal oxides [30] and metal-exchanged zeolites like ZSM-5 [31]. Of these, the transition metal oxides have advantages of high activity at low-temperatures, environmentally acceptable handling and disposal, and cost effectiveness [20,28].

Manganese oxides (MnO_x) have displayed excellent initial deNO_x performance at low-temperatures; for example, Mn/β -zeolite had 97.5% NO conversion at 240 °C [32]. Iron-based catalysts also have high deNO_x activity, and very low toxicity compared to V_2O_5 - WO_3 (MoO_3)/ TiO_2 catalysts [20,33]. Ren et al. [6] showed that pure Fe_2O_3 exhibited 95% NO conversion although the operation temperature window was toward a higher range of 250 °C to 400 °C. Supports for these transition metal catalysts have been inert metal oxides, such as Al_2O_3 , TiO_2 , and SiO_2 [34–36] that promote high temperature resistance and mechanical strength [12]; as a downside, some of these have exhibited low surface areas which decreases activity [32]. Using carbon-based supports has also been attempted because of the potential for high specific surface areas (like in activated carbon—AC), the ease of modifying their surface properties and chemical stability [34,37], attractive porosity and relatively low costs [12,38].

The use of C_2H_4 as the reductant for MnO_x -based deNO_x catalysts supported on AC showed NO conversions up to 100% at a temperature as low as 130 °C [39]. However, these mono-transition metal catalysts usually suffered from rapid deactivation; for example, the NO conversion over a 3.0 wt.% Mn/AC catalyst decreased by 70% after about 2 h of reaction testing [37]. Yang et. al. [37] studied the deactivation mechanisms of a CuO_x/AC catalyst during C_2H_4 -SCR reactions and found that the active metal oxide phase changed along with component aggregation that were attributed to catalyst deactivation. Tang et. al. also obtained more than 90% NO_x conversion at 150–250 °C with MnO_x/AC in NH_3 -SCR [37].

The development of commercial transitional metal-based HC-SCR catalysts is still in an early stage, especially for catalysts using AC supports. Hence, in this study, mono-transition metal oxides, i.e., MnO_x or FeO_x , and their mixtures were supported on a commercial AC and tested for NO conversion activity during C_2H_4 -SCR reactions at temperatures below 200 °C; the freshly-prepared and reaction-tested catalysts were then analyzed using bulk and surface sensitive techniques to determine structural and chemical aspects relating to their activity and deactivation.

2. Experimental

2.1. Catalyst Preparation

The activated carbon was purchased from Wanlong company, and had a particle size of 1000–2360 μm . It was treated with 10% HNO_3 for 4 h at room temperature, and then was washed with distilled water until the effluent pH became neutral; this AC was then dried at 140 °C for 14 h. It is denoted as nitric treated activated carbon (NAC).

The precursors used for impregnating MnO_x and FeO_x were $\text{Mn} \cdot (\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The NAC supports were impregnated with these solutions to achieve approximate Mn or Fe loadings of 3.0 wt.%, 5.0 wt.%, and 7.0 wt.% during which time the mixtures were sonicated in a bath for 2 h. After the mixtures were allowed to stand for 12 h, they were dried at 110 °C in a vacuum oven and then calcined at 400 °C for 2 h in a sealed muffle furnace under N_2 atmosphere. The synthesized materials were labeled as XMn/NAC , XFe/NAC where ($\text{X} = 3, 5, 7$).

The NAC was impregnated with an appropriate concentration of mixed precursor solution to achieve specified iron and manganese loadings within an ultrasonic bath for 2 h at room temperature. Then, the mixtures were allowed to stand for 12 h, after which they were dried in a vacuum oven at 110 °C and calcined at 400 °C for 2 h in a sealed muffle furnace under N_2 atmosphere. The synthesized catalysts were labeled as $\text{XFe3Mn}/\text{NAC}$, where ($\text{X} = 0, 1.0, 1.5$).

2.2. Catalyst Characterization

The catalysts were characterized to elucidate their physical and chemical properties before and after reaction testing. Surface areas and porosities were measured using a Micromeritics ASAP 2020 (ASAP 2020, Micromeritics Instrument Corporation, Norcross, U.S.A.) in which each sample was degassed overnight at 160 °C and then subjected to isothermal N₂ adsorption–desorption measurements at 77 K. Crystalline structures were examined by X-ray diffraction (XRD) using Cu K α irradiation in a Rigaku SmartLab system with a 2 θ range of 10–75°. Microstructures were investigated using scanning electron microscopy (SEM). The SEM imaging was performed on a FEI Quanta 250 embedded with a Bruker Quantax energy dispersive spectrometer (EDS). Molecular speciation was examined using Raman spectroscopy (Horiba-Jobin Yvon LabRam HR) at a spectral resolution of 2 cm^{−1} while using 442 nm laser excitation to minimize sample fluorescence. The laser light was focused on the samples with a confocal microscope with a 50 $\times$ objective (Olympus BX-30-LWD, NA = 0.5); the wavenumber calibration was checked using the silica vibrational mode at 520.7 cm^{−1}. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250Xi instrument (Thermo Fisher, Waltham, U.S.A) with Al K α excitation. The spectra were calibrated using the ubiquitous C1s peak at 284.8 eV.

2.3. Bench-Scale Testing for Catalytic Activity

The experimental setup for catalytic testing is shown in Figure 1. Ten grams of each sample was placed in a fixed-bed quartz tube reactor (i.d. = 20 mm) which was externally heated by a temperature-controlled furnace. Gas flow rates were controlled by mass-flow controllers (MFCs, MF SHY 400, SHY company, Suzhou, China), with the simulated gas mixture regulated to 500 ppm NO, 500 ppm C₂H₄, 3.0 vol.% O₂ and N₂ as the balance flow with a total flow rate of 1500 ml/min. Gas mixtures were injected into the reactor after catalyst temperatures reached a stable set point for each test. Inlet and outlet gas concentrations of NO and NO_x were analyzed by a flue gas analyzer (MRU, NOVA Plus, Heilbronn, Germany). From these data, the catalytic activities were calculated according to the following equation:

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

where the subscripts in and out indicate the inlet and outlet concentrations, respectively.

Figure 1. Schematic of the bench-scale setup.

3. Results and Discussion

3.1. Catalytic Performance

The NO conversion data versus time at different temperatures are shown in Figure 2 while using the 3Mn/NAC catalyst. It was used to provide baseline data that could be compared with previously published data [39]. Nearly 100% NO conversion occurred during the first 20 min at all temperatures (150 °C, 180 °C and 200 °C), but it suffered rapid declines after this initial period and showed less than

20% conversion after 2 h of testing. The temperature dependence of the activity followed the order of $150\text{ }^{\circ}\text{C} > 180\text{ }^{\circ}\text{C} > 200\text{ }^{\circ}\text{C}$.

Figure 2. Catalytic performance of 3Mn/NAC using C_2H_4 reductant. The reaction temperatures were 150, 180, and $200\text{ }^{\circ}\text{C}$, and the reaction conditions were 500 ppm NO, 500 ppm C_2H_4 and 3.0 vol.% O_2 at a total flow rate of 1500 ml/min.

The NO conversion testing data for XFe/NAC ($X = 3, 5$ and 7%) at $150\text{ }^{\circ}\text{C}$ are presented in Figure 3. Similar to the 3Mn/NAC data in Figure 2, the NO conversion declined dramatically after 15–20 min; it then leveled to values near 20% after about 80 min of testing, similar to the data for 3Mn/NAC. The Fe concentration had no significant effect on overall NO conversion. In summary, mono-metal oxide of either MnO_x or FeO_x on NAC had initial high NO conversion that was followed by rapid declines in activity after only 15–20 min from the beginning of reaction testing.

Figure 3. Catalytic performance of XFe/NAC ($X = 3, 5, 7$) using C_2H_4 as a reductant. The reaction temperature was $150\text{ }^{\circ}\text{C}$, and the reaction conditions were 500 ppm NO, 500 ppm C_2H_4 and 3.0 vol.% O_2 with a total flow rate of 1500 ml/min.

Figure 4 displays NO conversion data for the mono-metal oxides of 3Fe/NAC and 3Mn/NAC, and the bimetallic oxides 1.5Fe3Mn/NAC and 1.0Fe3Mn/NAC versus time at a $150\text{ }^{\circ}\text{C}$ reaction temperature. The bimetallic oxide catalysts had high initial activity and significantly better conversion maintenance than did the mono-metal oxide catalysts. Some deactivation was still evident for the bimetallic oxide catalysts after 2 h, however, the improvement in longer-term performance was evidence for synergistic effects between the Fe and Mn species.

Figure 4. Catalytic performance of X/NAC (X = 3Mn, 3Fe, 1.5Fe3Mn and 1.0Fe3Mn) using C_2H_4 as a reductant. The reaction temperature was 150 °C, and the reaction conditions were 500 ppm NO, 500 ppm C_2H_4 and 3.0 vol.% O_2 with a total flow rate of 1500 ml/min.

The difference between NO_x and NO of all tested catalysts was very small and was near 0% during the first 20 min of testing, and remained at less than 1–5 ppm during the entire tests. The blank experiment showed that NAC support contributed a very small number of NO conversion, which was less than 2%, which was not discussed while nearly 90% NO conversion was achieved.

Compared with current commercial SCR catalysts, the present studied Fe-Mn-catalyst was in poor stability. Deactivation is the common problem for low temperature HC-SCR catalysts, thus ease of deactivation is the key of this study. The excited and interesting phenomena have been observed during such preliminary study, especially, the Fe-Mn-catalyst with C_2H_4 exhibited a promoted performance.

3.2. Active Components Dispersion

Surface morphologies of the catalysts were investigated by SEM and SEM-EDS to examine whether dispersion changes of MnO_x and FeO_x species were related to rapid conversion declines or maintenance. The SEM images of HNO₃ treated AC, i.e., NAC without metal oxides, and of freshly prepared 1.5Fe3Mn/NAC in Figure 5 show readily accessible porous structures not noticeably changed as a consequence of incorporating the Fe and Mn oxides. In fact, as presented in Table 1, the surface areas and pore volumes of the NAC and metal oxide-containing catalysts were very similar to each other and near 650 m²/g and 0.4 cm³/g, respectively, before and after reaction testing (the as-purchased AC, before HNO₃ treatment, had a surface area of 710 m²/g). Maintenance of the porous structure may have been beneficial for dispersing the active species or maintaining an effective pathway for access of reactants and products to and from the active sites; however, the surface areas and porosities of the mono-metal 3Mn/NAC also did not significantly change before and after reaction testing although its NO conversion activity rapidly declined after 15–20 min of testing. Hence, catalyst surface areas and porosities did not control NO conversion for these catalysts, in agreement with previous studies showing the surface area of supported MnO_x catalysts was not a main cause of catalytic activity change during HC-SCR reactions [40].

(a) HNO₃ treated active carbon (NAC)(b) Fresh 1.5Fe₃Mn/NAC**Figure 5.** SEM images of NAC and fresh 1.5Fe₃Mn/NAC.**Table 1.** Surface area and porosity.

Samples	BET Surface Area (m ² /g)	Average Pore Width (nm)	Pore Volume (cm ³ /g)
3Mn/NAC before reaction testing	668.5	2.5	0.4
1.5Fe ₃ Mn/NAC before reaction testing	675.3	2.4	0.5
3Mn/NAC after reaction testing	632.6	2.4	0.4
1.5Fe ₃ Mn/NAC after reaction testing	658.5	2.4	0.4

The dispersions of MnOx and FeOx on NAC were further investigated by SEM-EDS mapping. These data for as-prepared 1.5Fe₃Mn/NAC, Figure 6 show the Mn signal was evenly distributed over the entire surface that was imaged while the Fe signal had slightly less of an even distribution. These data suggest that before reaction testing the MnOx and FeOx are mostly distributed uniformly on the NAC surfaces.

Elemental concentrations were also acquired using EDS data, a spectrum for which is displayed in Figure 7 along with the elemental concentrations. These concentrations were very close to the preparation concentrations of 1.5Fe and 3Mn.

(a) Distribution of Mn

(b) Distribution of Fe

Figure 6. Element distribution of Mn and Fe for the fresh 1.5Fe₃Mn/NAC catalyst.

Figure 7. Spectra of elements and their mass contents for fresh 1.5Fe₃Mn/NAC catalyst obtained by SEM-EDS.

3.3. Promotion Mechanism of FeO_x Addition

3.3.1. Physical Properties Evolution

The SEM-EDS acquired Fe and Mn elemental distributions for 1.5Fe₃Mn/NAC after reaction testing, as shown in Figure 8. Some agglomeration of Fe and Mn distributions can be found as compared to the distributions within the as-prepared catalyst in Figure 6. These Fe agglomerates are seen in the bright contrast areas on the catalyst surfaces toward the right and lower sides of the distribution maps. Agglomeration of Mn is also shown in Figure 8c but its extent is less than that observed for Fe. Hence, as compared to the EDS elemental distribution maps in Figure 6 of the as-prepared 1.5Fe₃Mn/NAC catalyst, the EDS data from tested catalysts indicated more Fe and Mn agglomeration. These aggregates could represent agglomeration sites of the originally active catalytic components, and thereby greatly affect active site dispersion to cause rapid deactivation. However, although this agglomeration was less than that observed for MnO_x species in previously published data on a reaction tested 3Mn/NAC catalyst [39], its activity had decreased to near 20% NO conversion after 120 min of testing whereas the activity of 1.5Fe₃Mn/NAC at the same time was near 80% NO conversion. Thus, their presence did not significantly affect the catalytic performance but still cause a NO conversion drop during 2 h testing.

Figure 8. Element distributions of Mn and Fe for 1.5Fe3Mn/NAC catalyst after reaction; two different samples were extracted from the tested catalyst after 120 min of testing and then examined via SEM-EDS.

3.3.2. Interactions between Fe and Mn Oxides

XRD data from 1.5Fe3Mn/NAC are presented in Figure 9 in which the main peaks have been identified. The broad peaks at $2\theta = 24^\circ$ and $2\theta = 43^\circ$ (labeled as A) are in agreement with those of amorphous carbon [41]; their positions and widths were the same in the fresh and tested catalysts, pointing to the stability of the NAC amorphous structure. Three other peaks at $2\theta = 33.5^\circ$, $2\theta = 35.1^\circ$, and $2\theta = 54.3^\circ$ (labeled as B, C and D, respectively) were present in both the fresh and tested catalysts, and were not significantly altered in position or peak intensities as a result of reaction testing. The peaks at $2\theta = 33.5^\circ$ (peak labeled as B) is attributed to Fe_2O_3 [42] and peaks at $2\theta = 35.1^\circ$ and 54.3° are attributed to $\text{Fe}_3\text{Mn}_3\text{O}_8$ [43]; although the intensities and widths of these Fe-related peaks were the same in the fresh and tested catalysts, it is rather difficult to determine whether Fe and Mn crystallinities have changed during testing because the XRD peaks are weak. Nevertheless, incorporating FeOx with

the MnOx did cause the formation of $\text{Fe}_3\text{Mn}_3\text{O}_8$ solid solutions which may be an active species in the FeOx-MnOx/NAC catalysts for NO conversion [43,44].

Figure 9. XRD spectra of 1.5Fe3Mn/NAC catalyst before and after reaction testing.

Raman spectra from 1.5Fe3Mn/NAC were also acquired before and after reaction testing, as shown in Figure 10. The spectrum of the fresh catalyst contained bands at 1360 cm^{-1} (labeled D), 1610 cm^{-1} (G) and triplet structured bands near 3000 cm^{-1} (2D); these are attributed to the activated carbon support [40] and are present with similar intensities in the reaction tested catalyst. A peak at 650 cm^{-1} in the as-prepared catalyst is attributed to Fe-O-Mn bond vibrations [45]; this band also was observed in the reaction tested catalyst but is narrower and higher in intensity. The narrowing of this band after testing suggests a higher degree of order or crystallinity in the $\text{Fe}_3\text{Mn}_3\text{O}_8$ species than before testing. Increased crystallinity as a result of testing points to a reordering or redistribution of the FeOx and MnOx species, a result also suggested by the SEM-EDS data from the as-prepared and tested catalysts. This redistribution would decrease the availability of active catalytic sites and could cause decreased NO conversion at the longer reaction times near 2 h.

Figure 10. Raman spectra of 1.5Fe3Mn/NAC catalyst before and after reaction testing.

The XPS spectra of Mn2p, Fe2p, O1s and curve fittings to their peak envelopes of 1.5Fe3Mn/NAC before and after reaction testing are presented in Figure 11. The Mn spectra showed two main peaks at 641.6 and 653.3 eV, corresponding to Mn 2p_{3/2} and Mn 2p_{1/2}, respectively [46]. For Fe, the peak envelopes were at 711.1 and 724.6 eV, corresponding to Fe 2p_{3/2} and Fe 2p_{1/2} and have multiple shoulders within their envelopes that signify more than one Fe species; their satellite peaks were at 719.1 eV and 733.3 eV [47]. The O1s peaks were asymmetric and were deconvoluted into two symmetric peaks at 530.0 and 531.8 eV; these were assigned to lattice oxygen and absorbed oxygen, respectively [46].

Deconvolution of the Mn and Fe XPS data point to three Mn species, including Mn⁴⁺, Mn³⁺ and Mn²⁺, and three Fe species, including one Fe²⁺ and two Fe³⁺ species, respectively [46]. The XPS spectra of Mn, Fe, and O from the catalyst were relatively stable for both the fresh and reaction tested samples, but some small changes were observed. For example, after testing the percentage of Mn⁴⁺ dropped from 19.5% to 13.5% and the Mn³⁺ increased by about 6.9%, while the percentage of Fe²⁺ increased from 8.4% to 12.5%. However, the change of valence distribution for Mn and Fe after reaction were relatively small, and the Fe-Mn synergistic effect may help to stabilize the composition.

Figure 11. XPS spectra and fitted peaks for catalyst 1.5Fe₃Mn/NAC.

4. Conclusions

The use of mixed oxides of Fe and Mn impregnated onto activated carbon was shown to significantly improve catalytic activity and activity maintenance for decomposing NO with C₂H₄ as the reductant in comparison to the mono-oxides of FeO_x and MnO_x supported on activated carbon when temperatures were less than or at 200 °C. Reasons for these differences were sought by acquiring

data from the as-prepared and reaction tested catalysts by surface and bulk analytical techniques, including BET surface area, porosity and pore volume analyses, SEM-EDS, XRD, Raman spectroscopy, and XPS. Overall surface areas, porosities and pore volumes of the supported mono-oxide or mixed metal oxide catalysts did not change as the concentrations of FeOx and MnOx were increased, and no difference existed between the as-prepared and tested catalysts. The SEM-EDS data indicated agglomeration of the FeOx and MnOx species in the mono-metal oxide catalysts during reaction testing while less, although some agglomeration, occurred in the mixed metal oxide catalysts after reaction testing. This difference agreed with the higher 80% NO conversion after 120 min of testing for the mixed metal oxide as compared to only 20% NO conversion at the same time for the mono-metal oxide catalysts. Simultaneously, the XRD and Raman spectroscopic data showed Fe₃Mn₃O₈ was formed during mixed metal oxide catalyst synthesis, and this compound was also identified in the reaction tested mixed metal oxide catalysts. This compound had higher crystallinity or ordering after reaction testing according to the Raman data, a factor which would decrease NO surface active sites and, thereby, decrease catalytic activity. Overall, the study supports the potential to synthesize active and stable HC-SCR catalysts for low temperature applications that are highly compatible with catalyst placement in reactor zones free of the deleterious gas phase species that occur in higher temperature reaction zones currently needing to be used for NH₃-SCR catalysts.

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