Annealing Strategies for the Improvement of Low-Temperature NH$_3$-Selective Catalytic Reduction Activity of CrMnO$_x$ Catalysts

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ABSTRACT: Annealing strategies for the citrate complexation–combustion method have been explored as a simple approach for improving the catalytic activity of mixed Cr–Mn oxides for the NH$_3$-selective catalytic reduction of NO$_x$. Materials prepared at 300 and 400 °C possess largely amorphous structures, consistent with highly dispersed Cr/Mn components. Annealing at 300 °C for 10 h facilitates the formation of catalysts possessing the largest surface area, reducibility, acidity, and activity window (92–239 °C), while areal activity is measured at 3.8 nmol s$^{-1}$ m$^{-2}$ and is comparable to values obtained for materials prepared at 400 °C. Conversely, shorter annealing times of 1 and 5 h at 300 °C produce materials that transform NO$_x$ about 2–3 times faster at equivalent surface area. Characterization demonstrates that simple annealing strategies have significant impact on the physicochemical and textural properties of these materials. Moreover, reducibility, O$_x$ species, and acidity were correlated against areal activity, but only the latter exhibited a near-linear correlation, indicating its dominance in controlling surface reaction rates.

1. INTRODUCTION

Rapid industrial development coupled with the increasing demand and consumption of petrochemical products has led to substantial increase in atmospheric nitrogen oxides (NO$_x$: NO, NO$_2$, and N$_2$O). The aforementioned emissions generate acid rain, photochemical smog, and, in some instances, possess a greenhouse effect more significant than CO$_2$. Combustion control and flue gas treatment techniques have both been previously examined for their potential as a means of controlling the emission of NO$_x$. They are relatively low-cost approaches, which abate emissions at source, consequently requiring minimal investment for process modification. However, their removal efficiency is modest and unable to meet increasingly stringent emission targets. Flue gas treatment has been explored via several methods, the most promising of which is catalytic NO reduction. The NH$_3$-selective catalytic reduction (NH$_3$-SCR) process is commonly associated with stationary emission sources, such as coal-fired power plants and oil refineries. The V$_2$O$_x$WO$_x$(MoO$_x$)/TiO$_2$ catalyst exhibits excellent activity and N$_2$ selectivity between 300 and 450 °C under typical commercial conditions. This temperature is consistent with that found before electrostatic precipitator and desulfurization units, which means that the catalyst is utilized in the presence of significant dust and SO$_2$ concentrations. To avoid such harsh operating conditions, the process could be located after the aforementioned devices at an operating temperature of 250 °C or lower. However, this concept requires the development of catalysts that are able to operate efficiently at the conditions detailed above.

Single-metal oxides have been explored for their potential in low-temperature NH$_3$-SCR processes, of which manganese oxides (MnO$_x$) are known to be one of the most promising. The combination of Mn with secondary transition-metal ions has led to the development of many active mixed-metal oxides, particularly, Ce–Mn, Fe–Mn, and Cr–Mn combinations. In each case, significant NO$_x$ conversions were obtained, but these values are attributable to the total surface reaction rate of the catalyst. Clearly, changes in surface area, activity, or their combination can influence conversion. As such, improvement of one property may offset a decline in the other, an effect that appears to be evident in previously reported Cr–Mn combinations. To confirm this possibility, areal activity is used to remove bias introduced by surface area from weighted activity (nmol s$^{-1}$ g$^{-1}$). Values of 2.2 and 5.2 nmol s$^{-1}$ m$^{-2}$

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were obtained for Cr(0.4)−MnO, and MnO₆, respectively.\textsuperscript{18} Clearly, the addition of Cr to MnO₆ inhibits the latter, indicating that improved conversion is obtained as a consequence of surface area enhancement. This also appears to be consistent with Cr−Mn materials prepared by Qiu et al. and Gao et al. (0.5 and 2.5 nmol s\textsuperscript{−1} m\textsuperscript{−2}, respectively).\textsuperscript{19,21} Chen et al. and Gao et al. produced materials possessing similar surface reaction rates, but different structures.\textsuperscript{18,21} In both cases, the citric acid method was employed, which could imply that the synthetic approach directly influences the generation of active sites. As such, modification of the annealing parameters may lead to improvement in areal activity while generating a range of Cr-Mn catalysts with varied physiochemical properties. Such an approach has been shown to readily modify both catalytic and material-type properties in other related systems.\textsuperscript{22,23} Mahnaz et al. reported that calcination temperature has a substantial impact on the primary manganese oxide phase formed over functionalized multiwalled carbon nanotubes. While higher temperatures notably increased the MnO fraction, longer hold time at 300 °C decreased the concentration of residual Mn(NO₃)₂.\textsuperscript{24} Bin et al. prepared Ti−Ce−V oxide catalysts at low and high annealing temperatures, with the former exhibiting significantly better chemisorption properties.\textsuperscript{25} Xu and co-workers reported that calcination had a significant effect on the catalytic activity of Ce−Zr composites, materials prepared at 500 °C possessed optimized Lewis acidity, active oxygen concentration, redox properties, and activity.\textsuperscript{26} Meng et al. prepared a series of Sm−Mn mixed oxides between 350 and 650 °C, yielding materials ranging from amorphous to crystalline. The precursor (15.00 g) was split into 8 batches, materials were homogenized in an in-house fabricated cylindrical mixing device. The precursor (15.00 g) was split evenly into two heavy-duty α-alumina crucibles without lids, placed into a muffle furnace, heated to the desired temperature at 2 °C min\textsuperscript{−1}, and held for a specified time. Upon cooling, the crucibles were removed from the furnace and the as-obtained powders were mixed. For the purposes of reaction testing, the catalysts were ground to a fine powder, pressed to 98 000 kN between 13 mm die, and then sieved to 60−80 mesh. Catalysts prepared at 300 and 400 °C are labeled as a and b, where a is the annealing temperature in °C and b is the hold time in h. Materials prepared at 450 and 650 °C are denoted by the final annealing temperature and time only; however, both were pretreated at 300 °C for 1 h to control the combustion process. Single oxides are denoted as Cr-300 and Mn-300, corresponding to their element and preparation temperature (°C); in both cases, hold time (1 h) was omitted for brevity.

2. Characterization. Powder X-ray diffraction (XRD) patterns were collected on a D8 Advance diffractometer (Bruker, Germany) with Cu Kα (λ = 1.5418 Å) radiation from 5 to 80° at 0.04° s\textsuperscript{−1}. Raman spectroscopy was carried out using a catalyst powder on a LabRAM Aramis (HORIBA Jobin Yvon, France) with a 532 laser (λ = 532 nm) and an electrically cooled CCD detector. In all tests, the microscope magnification was set at 50X with a resolution of 1 px\textsuperscript{−1}. Fourier transform infrared (FTIR) spectroscopy was performed on a Tensor 27 (Bruker, Germany) with a DLA TGS detector and a He-Ne laser. The background was obtained by scanning dried KBr powder, and the results are the average of 64 scans with a resolution of 4 cm\textsuperscript{−1} and are background-corrected. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were conducted in an SU8220 microscope (Hitachi, Japan), employing a cold field emission electron gun. Images were recorded via the upper detector for secondary electrons at an accelerating voltage of 10.0 kV and 5000−80 000 times magnification. The catalyst powder was placed onto the conductive adhesive and tested without sputtering. N₂ sorption isotherms were obtained on a Tristar II 3020 (Micromeritics), and surface area was calculated via the Brunauer−Emmett−Teller equation. About 100 mg of 60−80 mesh catalyst was pretreated at 150 °C under vacuum (50−100 mTorr) for 5 h to remove moisture and adsorbed gases. In all cases, the materials were tested multiple times and the reported values are the average. CHN elemental analysis was conducted on a Vario EL cube (Elementar, Germany) by heating preweighed powder samples (6.5 ± 0.2 mg) in the presence of O₂ to 1150 °C. A TCD was used for the quantification of CO/CO₂, H₂O, NOₓ, and N₂O, which are back-calculated to yield weighted values. Reported numbers are the average of two to three replicates, which are required to average out any sample heterogeneity. Thermogravimetric analysis (TGA) was performed on a TG 209 F3 Tarsus (Netzsch, Germany). Experiments were conducted between 50 and 650 °C at 5 °C min\textsuperscript{−1} with 6−7 mg of citrate precursor and a gas mixture composed of 20 mL min\textsuperscript{−1} air and 20 mL min\textsuperscript{−1} N₂. H₂-temperature programmed reduction (H₂-TPR) was performed on an AutoChem II 2920 Chemisorption Analyzer (Micromeritics). A 60−80 mesh catalyst (50 mg (±2 mg)) was pretreated in He (30 mL min\textsuperscript{−1}) at 200 °C for 1 h. After cooling to 50 °C, 10% H₂−Ar was introduced over the catalyst (30 mL min\textsuperscript{−1}) for 2 h to ensure that the results were not affected by H₂ adsorption at low temperature. Reduction was then conducted from 50 to 550 °C under the same H₂ flow at 10 °C min\textsuperscript{−1}. NH₃-temperature programmed desorption (NH₃-TPD) was undertaken on a TP 5080 (Xianquan, China). Approximately 100 mg of catalyst powder was pretreated at 200 °C for 1 h in N₂ (30 mL min\textsuperscript{−1}) and
cooled to 30 °C. 10% NH₃ in N₂ was passed over the clean catalyst surface at 30 mL min⁻¹ until complete surface saturation was achieved (1 h was found to be optimal). The NH₃-adsorbed catalyst was conditioned at 70 °C in N₂ (30 mL min⁻¹) to remove physisorbed species before heating at 10 °C min⁻¹ to 800 °C. An independent series of background experiments were conducted with a representative fraction of each catalyst, the purpose of which was to ensure that any thermally induced phase transitions could be reliably removed from the data. In situ DRIFTS was performed on a Vertex 70 FTIR spectrometer (Bruker, Germany) equipped with a smart controller, a liquid N₂-cooled MCT/A, and a Pike programmable temperature controller. Materials were pretreated at 200 °C for 1 h in N₂, followed by exposure of the catalyst surface to 0.1% NH₃ in N₂ for 0.5 h at 100 °C. At all stages of the experiment, the flow rate was maintained at 100 mL min⁻¹. The results were recorded after subtracting the background spectrum at reaction temperature and are an average of 64 scans obtained with a resolution of 4 cm⁻¹. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was performed on an OPTIMA 8000 (PerkinElmer). Test solutions were prepared by dissolving 100 mg of sample, yielding a stock solution of approximately 1000 mg L⁻¹, which is further diluted to 10 mg L⁻¹. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 Xi (Thermo Fisher Scientific) with Al Kα (E = 1486.6 eV) as the X-ray source. Initial survey scans have been conducted at a constant pass energy of 100.0 eV with a step size of 1.00 eV, while high-resolution scans were performed at 20.0 and 0.05 eV, respectively. Cr and Mn deconvolution were conducted by following reported methods, which were designed to model the complex peak shape of metal oxides.²⁷,²⁸

2.3. Catalytic Evaluation. The resulting materials were probed for their activity in the low-temperature NH₃-SCR process in a fixed-bed reactor near atmospheric pressure under the following conditions: 0.1% NO, 0.1% NH₃, 3.0% O₂, and N₂ balance. Approximately 1.50 g of catalyst was used for each test, with an ambient flow rate of 1000 mL min⁻¹ generating a GHSV of approximately 50 000 h⁻¹. The propensity of Mn-based NH₃-SCR catalysts as adsorbents at low temperatures is well known,¹²,¹⁸ therefore, materials were equilibrated in the presence of the gas mixture at approximately 50 °C for 1 h prior to heating the reactor. Experiments were conducted from 80 to 240 °C at 20 °C increments with a ramp rate of 2 °C min⁻¹ via temperature control. The total NO concentration was continuously monitored by an Ecom EN2 gas analyzer; however, reported results were obtained at or near steady state. Two key parameters were used to assess the activity of these systems, NOx conversion and areal activity:

\[
CNO_x(\%) = \frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}} \times 100\%
\]

areal activity \[
= \frac{Q_{NO} \times CNO_x}{SSA \times \dot{m}_{cat}}
\] (2)

where CNOx is the conversion of NOx, [NOx] is the total concentration NO and NOx, and [NOx]_{in} and [NOx]_{out} were determined by measuring NOx via bypass reactor lines, respectively. Areal activity is expressed in nmol m⁻² s⁻¹, \(Q_{NO}\) is the molar flow rate of NO in nmol s⁻¹, NOx conversion at 100 °C is a dimensionless fraction, SSA is the specific surface area in m² g⁻¹ of the specified catalyst, and \(\dot{m}_{cat}\) is the weight used for the reaction in g.

3. RESULTS AND DISCUSSION

3.1. Characterization. XRD patterns were recorded for mixed Cr–Mn oxides prepared at temperatures ranging from 300 to 650 °C and single Cr/Mn oxides prepared at 300 °C (Figure 1). Cr-300 and Mn-300 exhibit patterns typical of cubic α-Cr₂O₃ and tetragonal Mn₃O₄, respectively.¹⁸,²¹,²⁹,³⁰

The former phase is relatively well crystallized, as indicated by the significant line intensity of the diffraction peaks near 25° and 34° and between 33° and 36° 20. 650-1 gives rise to a single well-defined phase that is consistent with CrMn₃O₄.³¹ The calculated cell parameter (a = 0.8475 nm) coincides very closely with that obtained by Priebe et al. (a = 0.8479 nm),³¹ suggesting a high degree of similarity between the two materials. The cell parameter for 450-1 (a = 0.8463 nm) is notably smaller than that above, while the obtained XRD pattern also exhibits α-Cr₂O₃ (Figure 1). Clearly, the expected CrMn₃O₄ phase is not fully formed at this lower temperature, instead it appears consistent with an as-yet undefined mixed-spinel phase. Materials synthesized at 400 °C produce very broad diffraction lines in a similar region to the spinels, which are consistent with crystallite sizes of 2.5–4.0 nm according to the Scherrer equation. Longer hold time facilitates the formation of α-Cr₂O₃, but this is a relatively minor crystalline phase. Preparation at 300 °C yields only a series of low-intensity lines regardless of hold time, indicating the highly amorphous nature of these materials.

Spectroscopic analysis (Figure 2) verifies that Mn-300 is composed of only the Mn₃O₄ phase identified by XRD. Curiously Cr-300 produces features consistent with both Cr₂O₃ and CrOOH,³² which suggests that the latter is present as a highly amorphous phase. Group theory predicts five Raman-active phonon modes (\(A_g\), \(E_g\), and \(F_{2g}\)) for the well-defined cubic spinel present for 650-1. However, the obtained spectrum (Figure 2A) is far more convoluted than that previously found for materials of the same symmetry, such as CoCr₂O₄.³³,³⁴ Priebe et al. proposed that CrMn₃O₄ takes on the following configuration: Cr(IV)Mn(II)Mn(IV)₃O₄, where Cr(IV) occupies tetrahedral positions and Mn(II)/ (IV) fill 1.5 octahedral sites. This structure possesses charge-
neutral defects, which lower space group symmetry and adjust the number of Raman-excited phonons. The FTIR spectrum (Figure 2B) reveals only two obvious signals, ca. 495 and 610 cm\(^{-1}\), which correspond to two of the four expected F\(_{1u}\) modes predicted by group theory. Those positions are identical to the ones obtained for Mn\(_3\)O\(_4\), an observation pointing toward similar contributions from oxygen in both structures. However, the tetragonal spinel produces another F\(_{1u}\) feature in the mid-IR range (∼410 cm\(^{-1}\)) that is associated with Mn\(^{3+}\) in the octahedral hole. This is lacking from spectra obtained for the cubic structure, suggesting that different species occupy the six-coordinate position. The sample prepared at 450 °C possesses similar spectra to 650-1, albeit shifted toward lower frequency. The only exception is the presence of FTIR features above 800 cm\(^{-1}\) that are consistent with higher-oxidation-state Cr species. Raman and FTIR spectra obtained for materials prepared at 300 and 400 °C are largely similar, while being significantly different from those described above. The relative line broadness suggests that these materials generally possess very low symmetry, while the FTIR spectrum of 400-10 (Figure 2B) reveals two additional bands around 415 and 440 cm\(^{-1}\), which match modes associated with crystalline Cr\(_2\)O\(_3\). Furthermore, a number of peaks evident in both Raman and FTIR spectra demonstrate that higher-valence Cr species are present in all amorphous systems. Spectroscopic investigations demonstrate clearly that materials prepared at 300 and 400 °C are highly similar, while crystalline phases evident for the latter are only minor components.

SEM images were obtained to examine the microstructure of amorphous Cr–Mn mixed-oxide catalysts (Figure 3). At 5000X magnification (inset of Figure 3), materials exhibit no distinct microscale morphology and possess very rough surfaces in all instances. Images obtained at higher magnification (80 000X) show that the bulk grains are composed of irregular-shaped particles of variable agglomeration degree. A similar observation reported by Deorsola et al. suggests that significant aggregation may be a trait of combustion-based synthetic processes. Furthermore, the variable size of the grain in each amorphous system makes it difficult to discern a clear correlation between annealing parameters and particle size. Instead surface area measurements are required to better understand the evolution of particles from the perspective of its textural properties. At 300 °C, a clear improvement in surface area is found between 1 and 10 h (31 and 116 m\(^2\) g\(^{-1}\), respectively), while minor variation is evident from 1 to 5 h (Table 1). Elemental analysis proves that

![Figure 2. (A) Raman and (B) FTIR spectra of CrO\(_x\), MnO\(_x\), and CrMnO\(_x\) catalysts: (a) Cr-300; (b) Mn-300; (c) 300-1; (d) 300-5; (e) 300-10; (f) 400-1; (g) 400-10; (h) 450-1; (i) 650-1.](image-url)

![Figure 3. SEM images of amorphous CrMnO\(_x\) catalysts: (a) 300-1; (b) 300-5; (c) 300-10; (d) 400-1; (e) 400-10, where the insets are lower-magnification images with a 5 μm scale.](image-url)
Table 1. Surface Area, Peak Area Ratio between Low- and High-Temperature Reduction Peaks, Relative Acidity, Acid Site Density, and Areal Activity of CrMnO$_x$ Catalysts$^a$$^b$

| catalyst | surface area (m$^2$ g$^{-1}$) | LT-HT$^c$ (au) | H$_2$ consumption (au) | relative acidity$^d$ (au) | acid site density (au) $10^{-2}$ | activity window$^e$ (°C) | $T_{opt}$ (°C) | areal activity (nmol s$^{-1}$ m$^{-2}$) |
|----------|-----------------------------|----------------|------------------------|---------------------------|-------------------------------|-----------------------------|----------------|-------------------------------------|
| 300-1    | 31 ± 5                      | 6.15           | 1.86                   | 1.00                       | 3.23 ± 0.62                  | 112-231                     | 101            | 8.6 ± 1.4$^h$ (4.6)                |
| 300-5    | 37 ± 6                      | 5.96           | 1.95                   | 1.39                       | 3.76 ± 0.72                  | 90-230                      | 83             | 11.5 ± 1.3$^h$ (6.5)               |
| 300-10   | 116 ± 4                     | 8.09           | 2.09                   | 1.64                       | 1.41 ± 0.05                  | 92-239                      | 81             | 3.8 ± 0.2$^h$ (2.3)                |
| 400-1    | 93 ± 3                      | 5.93           | 1.94                   | 1.01                       | 1.12 ± 0.00                  | 99-231                      | 87             | 4.1 ± 0.5 (2.2)                    |
| 400-10   | 77 ± 9                      | 3.82           | 1.64                   | 0.90                       | 1.17 ± 0.15                  | 109-231                     | 97             | 3.9 ± 0.7 (2.2)                    |
| 450-1    | 73 ± 2                      |                |                        |                           |                              |                            |                |                                     |
| 650-1    | 35 ± 2                      |                |                        |                           |                              |                            |                |                                     |
| 650-3$^a$| 70                          | N/A            | N/A                    | N/A                       | N/A                          | 100-N/A                     | 87             | 2.2 (--)                           |
| Cr(0.1)$^a$ | 154                     | N/A            | N/A                    | N/A                       | N/A                          | 149-273                     | 117            | 0.5 (--)                           |

$^a$N/A: Not applicable. $^b$: Not determined. $^c$: Ratio between low-temperature (LT) and high-temperature (HT) H$_2$-TPR peak area from 100 to 500 °C. $^d$: Correlation of NH$_3$-TPD peak area between 120 and 700 °C relative to 300-1. $^e$: 80% conversion minimum. $^f$: Temperature at which 60% NO$_x$ conversion is achieved. $^g$: Calculated at 100 °C; brackets denote values at 80 °C. $^h$: Calculation made close to maximum conversion.

Table 2. Elemental Surface and Bulk Concentrations of CrMnO$_x$ Catalysts

| catalyst | Mn | Cr | O | surface Cr ratio | bulk Cr ratio | carbon concentration (wt %) |
|----------|----|----|---|-----------------|---------------|-----------------------------|
| 300-1    | 17.64 | 13.95 | 68.41 | 0.44 | 0.40$^i$ (0.41) | 0.37 ± 0.07 |
| 300-5    | 18.12 | 13.57 | 68.31 | 0.43 | 0.40 (0.40) | 0.24 ± 0.05 |
| 300-10   | 17.94 | 13.50 | 67.56 | 0.45 | 0.40 (0.40) | 0.25 ± 0.05 |
| 400-1    | 18.02 | 13.76 | 68.22 | 0.43 | 0.40 (0.42) | 0.24 ± 0.05 |
| 400-10   | 19.69 | 12.65 | 67.66 | 0.39 | 0.39 (0.39) | 0.27 ± 0.05 |

$^i$: Determined by ICP-AES; brackets denote values determined via EDX.

The nature of this feature is highly subjective, but is not consistent with the removal of trace carbon from materials after treatment at 400 °C (Table 2). Interestingly the aforementioned mass loss occurs within the same thermal range as the transition from amorphous to crystalline (400-1 and 450-1, respectively), ergo a connection between the two processes is implied. Under temperature-controlled conditions, it is clear that complete citrate removal is not achieved at 300 °C; however, this does not fully replicate synthetic conditions. Experiments conducted with well-established hold times (Figure 4) demonstrate that a small residual mass remains after treatment for 60 min. Interestingly, only 90 min were required to reach a final mass consistent with that obtained before 425 °C. Therefore, the finite combustion time scale ensures that particles prepared at 300 °C for 5 and 10 h evolve as a consequence of annealing conditions and not due to secondary effects. Materials prepared at 400 °C avoid the uncertainties of incomplete combustion (Figure 4 and Table 2). As such, the observed surface area decline from 93 to 77 m$^2$ g$^{-1}$ between 1 and 10 h, respectively, is wholly associated with thermally induced transformation. Interestingly, 450-1 exhibits a similar value (73 m$^2$ g$^{-1}$) to that obtained for 400-10, implying that variations of temperature and hold time can yield similar textual properties. Obviously, this does not extend to the formation/crystallization of the CrMnO$_x$ spinel structure, which appears to be thermally dependent.

ICP-AES and EDX analyses (Table 2) reveal that the Cr ratios obtained for all amorphous materials are very close to those anticipated from the experimental design (0.40). Obviously, if any losses are evident during the synthetic approach, then they do not favor one element over another, allowing for the observed consistency. Strictly speaking, ICP is more representative of the bulk due to the significantly larger...
Figure 5. Elemental mapping of amorphous CrMnO\textsubscript{x} catalysts: (a) 300-1; (b) 300-5; (c) 300-10; (d) 400-1; (e) 400-10.

Figure 6. High-resolution Mn 2p (A), Cr 2p (B), and O 1s (C) XPS scans of CrMnO\textsubscript{x} catalysts: (a) 300-1; (b) 300-5; (c) 300-10; (d) 400-1; (e) 400-10 (For full color images, the reader is referred to the online version.).
quantity of material analyzed by the technique. Thus, it is not surprising that EDX, an approach that analyzes individual micron-sized particles, yields slightly greater deviation (0.39–0.42 vs 0.39–0.40). Elemental mapping (Figure 5) reveals that the materials do not possess regions that are highly concentrated in only one element. In all examples, Mn and Cr components are highly dispersed throughout the particle on the microscale. As such, the catalysts are believed to take the form of an amorphous mixed-oxide structure, one that appears to be different from other reported Cr–Mn combinations.18,19,21

Surface composition (Table 2) indicates that all materials, except 400-10, are somewhat enriched with Cr compared to the bulk (0.43–0.45 vs 0.40). High-resolution Mn 2p spectra (Figure 6A) show the presence of two distinct signals at 653.8 ± 0.1 (2p1/2) and 642.2 ± 0.1 (2p3/2). The obtained energy separation, 11.6 eV, is consistent with values previously reported for mixed manganese oxides.27,28 To rationalize the nature of the Mn component, peak fitting deconvolution was conducted for both Mn signals.27,28 Three dominant valence states emerge, coinciding with variable proportions of Mn(II), Mn(III), and Mn(IV). In general, all systems possess a significant quantity of Mn(III), while modest values of the other two species are found (Table 3). A clear trend emerges with annealing time at 300 °C, where the concentrations of Mn(II) and Mn(III) decrease and the Mn(IV) fraction increases. Comparative examination of 300-1 and 400-1 demonstrates that higher temperature increases both Mn(II) and Mn(IV) surface concentrations. Two obvious peaks are observed in the high-resolution Cr 2p spectra (Figure 6B) at around 586.3 ± 0.1 and 576.8 ± 0.1 eV, typical of the 2p1/2 and 2p3/2 signals, respectively. Following the deconvolution protocols reported by Biesinger et al.,27 three distinct environments are evident, with two readily identified as Cr2O3 and Cr(VI). The other exhibits a similar peak splitting pattern to the Cr(III) species, albeit shifted toward higher binding energy. From the trends observed for MnOOH and Mn2O3ocr,29 we suggest that this additional feature may be consistent with Cr(III) ions in a CrOOH-type environment. The small energy separation between Cr(III) species does not allow for a definitive quantification of the two individual components; hence, their total is denoted as Cr(III) in Table 3. Three distinct oxygen species are apparent in the obtained O 1s spectra (Figure 6C), coinciding with adsorbed water (Ow), active oxygen (Oa), and lattice oxygen species (Ocr).35,42 The former is quite consistent between surfaces (Table 3), while the relative concentration of lattice oxygen is larger for 300–600, 400–60, and 400–600, implying that lower temperature and hold time is beneficial for the retention of more coordinatively unsaturated cationic species. Typically, active oxygen exists as a variety of functionalities, particularly, hydroxyls, adsorbed O− and O2−. In all cases, there is some precedent of their benefitting the low-temperature NH3-SCR process.20,43,44 The dominance of Cr(III) species in Cr-containing catalysts is not a particularly surprising result,41 but the large surface concentration of Mn(III) is in stark contrast to a number of other studies.38,44 However, the use of a more advanced modeling technique may more accurately reflect the surface composition than single-peak models.27,28 For example, Kang et al. found large concentrations of bulk Mn3O4 and Mn2O3 species (∼80.0%) for materials prepared at 350 and 450 °C. However, the surface Mn(IV) concentration was determined to be approximately 50% from a single-peak fitting model.45 It is also well documented that aqueous Mn(IV) ions readily oxidize Cr(III) even under ambient conditions.46,47 In these cases, there has been no evidence of charge carriers, implying that direct interaction between the two is required for the reaction to proceed. However, the degrees of freedom are significantly constrained in the solid-state compared to those above. Thus, the formation of undefined Cr–O–Mn bonding is likely required to meet the definition of direct interaction in solids. Previous observations over well-defined mixed-spinel structures have suggested that Cr(VI) preferentially forms at the surface of the catalyst.48,49 Therefore, Mn species meeting the bonding requirement within surface/subsurface layers may preferentially undergo reduction. Interestingly, the trends observed for Cr(VI) and Mn(IV) imply that annealing time does not significantly influence the proposed synergetic transition. Instead, the formation of undefined Cr–O–Mn bonding could arise during the combustion process, which drives the initial formation and equilibration of transition-metal valence states. H2-TPR profiles reveal the presence of two reduction signals for all materials within the explored range (Figure 7). The first maxima are observed around 275 ± 7 °C, while the second are obtained as shoulders at 365 ± 10 °C. However, there are deviations in total intensity (Figure 7) and the relative ratio between low- and high-temperature signals (Table 1). Tang et al. demonstrated that well-defined α-Mn3O4 exhibits two signals at approximately 350 and 450 °C. Their total area ratio is approximately 1–2 coinciding with the sequential reduction of Mn2O3 to MnO via the intermediate spinel phase.50 β-Mn3O4 also exhibits two peaks that are shifted toward lower temperature (310 and 410 °C), indicating improved reducibility of the Mn2O3 and Mn3O4 intermediates.51 The reduction positions observed for the Cr–Mn combinations (Figure 7) more closely resemble those of MnO2 albeit at lower temperature. Also, the intensity ratios obtained between low- and high-temperature peaks (Table 1) are very different from those reported for either manganese compounds.52,53 There are two key differences that could contribute to the

Table 3. Surface Oxidation States and Speciation of CrMnOx Catalysts

| Catalyst  | Mn 2p3/2 | Cr 2p3/2 | O 1s |
|-----------|----------|----------|------|
|           | Mn(II)   | Mn(III)  | Mn(IV) | Cr(III) | Cr(VI) | O5 | O6 | O7 |
| 300-1     | 20.7     | 70.8     | 8.6 | 90.9 | 9.1 | 51.0 | 41.3 | 7.7 |
| 300-5     | 19.8     | 67.3     | 12.9 | 89.8 | 10.2 | 52.1 | 39.1 | 8.8 |
| 300-10    | 17.7     | 67.9     | 14.5 | 87.5 | 12.5 | 55.2 | 37.6 | 7.2 |
| 400-1     | 22.8     | 64.6     | 12.6 | 90.0 | 10.0 | 55.9 | 35.8 | 8.3 |
| 400-10    | 23.3     | 65.8     | 10.9 | 91.5 | 8.5 | 55.9 | 35.2 | 8.9 |

aConcentration is uncertain due to possible in situ reduction in the measurement chamber.41
extent of the aforementioned ratio: the amorphous nature of the mixed material and the presence of high-oxidation-state Cr species. In the case of the former, it is plausible that negligible long-range ordering promotes a reduction of the M–O bond energy, an effect typically observed for smaller crystallites.\(^{52}\) Furthermore, the energetic distinction between surface and bulk M–O bonds should become less defined in smaller domains. While these arguments are qualitatively valid, they are unable to rationalize significant variations found for materials prepared at 300 and 400 °C. Therefore, Cr species must contribute to the observed TPR profiles, while being susceptible to modification during the synthetic process.

The feature observed at 275 °C lies within the range commonly considered for the reduction of Cr species,\(^{18,19,21,53,54}\) but definitive assignment is difficult. For Cr–Mn combinations, transitions in this range have been assigned to the reduction of Cr\(_2\)O\(_3\) to CrO.\(^{18,19,21}\) However, no empirical evidence has been provided to support the validity of this assignment. Other authors have suggested that Cr(III) reduces only at high temperature, while attributing the reduction of Cr(VI) to features ca. 250 °C.\(^{48,49,53,54}\) The Cr–Mn mixed-oxide catalysts clearly contain appreciable quantities of higher-oxidation-state Cr species. It is likely that the 275 °C peak is a combinative reduction feature, consistent with both higher-oxidation-state Mn and Cr components. The relevance of Cr(VI) species in NH\(_3\)-SCR appears to be highly dependent on the catalyst type and whether or not it is supported. For instance, Engweiler et al. reported that NH\(_3\) reacts with Cr(VI) to form a stable [Cr(I)–NO]\(^{2+}\) complex over TiO\(_2\)-supported Cr\(_2\)O\(_3\).\(^{55}\) While, Sloczynski has shown that coupling Cr(VI) with another redox-active metal can promote the conversion of NO\(_x\).\(^{48}\) Of these two examples, our amorphous catalysts more closely resemble the latter, implying that Cr(VI) species may play an active role in SCR catalysis. Several studies have demonstrated that increased NH\(_3\)-SCR activity typically correlates with improved reduction characteristics.\(^{16,45,56}\) In most cases, this is demonstrated by the shift of reduction maxima toward lower temperature, but there is little variation for our systems. However, changes in the total H\(_2\) consumption (Table 1) indicate semiquantitative variation in the total number of reducible species. A monotonous increase in the aforementioned value is realized for materials prepared at 300 °C with increasing annealing time, which demonstrates that the number and/or valence state of cationic species increases with longer exposure to oxygen. Interestingly, this trend is not reflected at 400 °C, instead a significant decline of the low-temperature peak is evident, indicating thermal sensitivity of higher-valence Cr species.\(^{49}\)

Acidity is also considered to be an important factor in the NH\(_3\)-SCR process, although it is often perceived as more relevant at higher temperature.\(^{56}\) It is important to recall that NH\(_3\)-TPD profiles do not just relate to “acidity”; in several cases Lewis acid sites are reducible surface species. Regardless, the specificity of this technique makes it most suited to probe the number of catalytically relevant sites. All amorphous materials exhibit largely similar profile shapes (Figure 7) with minimal variation in peak position, \(\alpha\): 330–345 °C, \(\beta\): 435–450 °C, \(\sigma\): 470–485 °C, and \(\eta\): 560–570 °C. Even with this similarity, the relative acidity changes significantly (Table 1), accurately mirroring the qualitative trend observed in the H\(_2\)-TPR profiles. These absolute trends reveal that 300-10 exhibits the largest number of acid sites, but each material possesses a significantly different surface area. Thus, shorter annealing time and lower temperature are more beneficial for maintaining acid site density, while 300-10, 400-1, and 400-10 all possess statistically similar values (Table 1). As such, the decrease in acidity at 400 °C can be rationalized as a simple decline in surface area, but it remains unclear why 300-10 cannot support higher site densities. To further probe the nature of adsorbed NH\(_3\) species, a series of in situ DRIFTS experiments were conducted (Figure 5). NH\(_3\) adsorption over 300-1 generates a relatively simple DRIFT spectrum between 800 and 1750 cm\(^{-1}\) at 100 °C (Figure 8). Weakly coordinated NH\(_3\) is observed between 960 and 990 cm\(^{-1}\). Lewis acid-bound NH\(_3\) is found at ca. 1220 and 1602 cm\(^{-1}\). NH\(_4^+\) formed on Bronsted acid sites occurs at 1445 and 1680 cm\(^{-1}\) (symmetric and asymmetric bending modes, respectively).\(^{57,58}\) Upon adsorption of NH\(_3\), a new acidic O–H stretching mode is formed (3630 cm\(^{-1}\))\(^{(59)}\), implying that the former dissociates over strong Lewis acid sites. Curiously, no corresponding amide rocking feature is found,\(^{60}\) suggesting that either the catalyst dissociates NH\(_3\) multiple times or the signal has shifted position. The NH\(_3\) Lewis acid site signal lowers in intensity and broadens for 300-5, demonstrating a change in the fundamental nature of the bending mode. Coupled to this is the presence of signal splitting in the N–H stretching region (2600–3400 cm\(^{-1}\)), consistent with change in the symmetry of the adsorbed NH\(_3\). Furthermore, for 400-1, the effects discussed above are exacerbated, implying a greater change.
in the nature of adsorbed species. The lowering of both vibrational and bending modes, in addition to a smaller acidic O–H signal, indicates that the bonding between NH₃ and Lewis acid sites becomes weaker. Consequently, the extent of NH₃ dissociation is lowered, generating more labile NH₃ species and improving the reversible adsorption properties for 300-5. However, higher preparation temperature clearly modifies the surface to a great extent, producing fewer acid sites of more varied nature (Figure 9).

![Figure 9. In situ DRIFTS of NH3 adsorption over CrMnOx catalysts: (a) 300-1; (b) 300-5; (c) 400-1.](image)

### 3.2. Catalytic Performance

Amorphous and crystalline Cr–Mn mixed-oxide catalysts were explored for their activity in the NH₃-SCR process with excess O₂ (Figure 10). It is apparent that the amorphous systems exhibit much larger conversion than either crystalline materials at temperatures less than 160 °C. Of all those tested, 300-10 produces the widest activity window and lowest T₆₀ value (Figure 10 and Table 1). Characterization results demonstrate that this catalyst possesses the largest surface area, total reducibility, and acidity, which match characteristics reported to be beneficial for the low-temperature NH₃-SCR reaction. One of the major drawbacks of the Cr–Mn combination appears to be inherently low surface reaction rates (areal activity). The “so-called” best-performing material in this study exhibits a value of approximately 3.8 nmol s⁻¹ m⁻², which is comparable to that obtained for materials synthesized at 400 °C (Table 1). This is somewhat higher than combinations reported by Chen et al., Qiu et al. (Table 1), and Sloczynski et al. (1.5 nmol s⁻¹ m⁻²) at 100 °C. However, 300-5, with significantly lower surface area (averaging 37 m² g⁻¹), possesses reaction-based metrics comparable to 300-10. Consequently, its areal activity is much higher, 11.5 nmol s⁻¹ m⁻², significantly improving upon previously reported values for Cr–Mn combinations.

Through the design of a systematic annealing strategy, a series of Cr–Mn catalysts possessing a range of physicochemical properties have been developed. To understand the fundamental nature of the observed enhancement effect, variations in reducibility, O₆ surface concentration, and acidity were considered alongside areal activity values. There are numerous examples showing that materials exhibiting improved SCR performance often possess enhanced redox properties. However, the minor variations observed for the amorphous materials do not give rise to a convincing correlation with areal activity (Figure 11A). This is further extended to H₂ consumption, which exhibits significant variation at nearly constant activity (Table 1). For the purposes of the NH₃-SCR reaction, the amorphous catalysts do not appear to be limited by their reduction properties. XPS-observed O₆ species are often associated with activated oxygen, which can facilitate the formation of NO₂, an important intermediate for the fast-SCR process. Much like reducibility, this trend also exhibits a volcano plot (Figure 11B). Although there is some sense to the trend, where higher O₆ concentration is observed for 300-1 and 300-5, its relevance is doubtful due to the effective concentration once surface area is considered. The signal attributed to O₆ corresponds to several different species, such as active oxygen and hydroxyl groups. The latter is more prevalent in 300-1 and 300-5, its relevance at 300 or 5 h hence is uncertain, requiring further study to explore the mechanistic aspects of these active systems.

### 4. CONCLUSIONS

A simple and low-cost annealing approach has been explored to improve the catalytic efficiency of CrMnOₓ mixed oxides for low-temperature NH₃-SCR. Characterization techniques show that all materials possess complex amorphous structures with minor crystalline phases evident at higher temperature. 300-10 possesses the largest surface area, reducibility, acidity, and number of high valence species, culminating in the highest NOₓ conversion at 100 °C. Annealing at 300 °C for 1 or 5 h

![Figure 10. NOₓ conversion of CrMnOₓ catalysts between 80 and 240 °C, where the dotted lines indicate 60 and 80% NOₓ conversion.](image)
facilitates the formation of materials with significantly larger areal activities, which is observed to be largely consistent with acid site density. 300-5, the largest surface reaction rate obtained in this study (11.5 nmol s$^{-1}$ m$^{-2}$), compares favorably to previously reported Cr–Mn combinations, affording a 5- to 23-fold increase, making this the most active CrMnO$_x$ catalyst to date. Additional investigations are currently ongoing to determine their activity under typical flue gas conditions, while also attempting to understand the importance of acid site nature on overall surface activity.

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Notes
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