Catalytic reduction of NO with H₂ over redox-cycling Fe on CeO₂

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Abstract: Removal of NO_x species from automotive emissions continues to be a challenge, particularly using replacements for Pt-group metals. Here, we demonstrate the synthesis of FeO_x domains on CeO₂ from the precursor Fe ethylenediaminetetraacetate (NaFeEDTA) and its utility in the reduction of NO with H₂ as a model reaction for tailpipe emissions. Diffuse-reflectance UV-visible and X-ray absorption near-edge spectroscopies indicate the formation of small, non-crystalline FeO_x domains. Using the EDTA precursor, TPR and *in situ* XANES show that up to 45% of the FeO_x centers were capable of undergoing redox cycles in H₂ up to 550°C, whereas only 23% of FeO_x centers derived from Fe(NO₃)₃ were redox active. Similarly, at comparable Fe surface densities, the FeEDTA-derived catalysts were more active than the nitrate-derived materials in the reduction of NO to N₂ (85-95% selectivity) with H₂ at 450°C. The presence of both the bulky organic ligand and the alkali are essential for the observed enhancements in fraction redox active and to achieve high NO reduction rates. Rates over all materials were fit to a single correlation against the number of redox-active FeO_x

centers, suggesting that these are the catalytic active sites. The new materials describe here may offer new avenues for emissions control without Pt-group metals or substituted zeolites.

Keywords: deNO_x; ceria; redox; emissions; XANES

1. Introduction

The removal of NO_x from automotive emissions continues to be an important challenge in heterogeneous catalysis. The current industry standard, the three-way catalyst, is a remarkable achievement in emissions control, but relies on scarce and costly noble metals such as Pd, Pt and Rh [1], hence an interest in catalysis by earth-abundant species. Metal exchanged zeolites have garnered academic and industrial interest as potential replacements due to their low cost and high activity in the removal of NO [2-12]. Much focus has been placed on Fe-exchanged ZSM-5 zeolite, in particular, due to its activity in NO reduction with NH₃ [4-7] and hydrocarbons [7-10] and high selectivity towards N₂ [7, 9]. One concern is durability in the presence of H₂O [10], which depends strongly on the framework. It is generally accepted that low nuclearity species are responsible for the catalytic behavior of Fe-exchanged zeolites. Isolated Fe ions [7, 8, 13], μ -oxo dimers [10, 11, 14], and oligomeric species [9] are potential active sites proposed in the literature.

Several studies have attempted to reproduce the active structures and reactivity of Fe exchanged zeolites on more common oxide supports. Incipient wetness impregnation (IWI) of oxide supports with Fe(NO₃)₃ solutions—ideal due to its simplicity and

scalability—produces a multitude of Fe structures on CeO₂ [15, 16], ZrO₂ [16, 17], and SiO₂ [16-19] even at fractions of monolayer coverage. Adsorption-precipitation of FeSO₄ produces a narrower distribution of surface species on SiO₂, but still is comparable to IWI of Fe(NO₃)₃ [20, 21]. Overall, structurally heterogeneous surfaces obscure the underlying chemistry and make difficult the development of fundamental insights. Advanced techniques involving chemical vapor deposition of FeCl₃ [22] or grafting of Fe siloxide precursors [23, 24] are more selective in producing dimers and monomers, but may be difficult to scale up.

Furthermore, similar FeOx structures on zeolitic and non-zeolitic supports need not display the same catalytic behavior. For example, supports like CeO₂ undergo redox cycles, store oxygen, and chemisorb H₂ [25, 26], all of which can influence the behavior of the surface FeOx species. Hence, the development of support-specific synthesis-structure-reactivity relations is a necessity, particularly on reducible supports.

Here, we demonstrate a route to FeOx surfaces species of controlled dispersion on CeO₂ based on prior work by some of the authors for the synthesis of FeOx-SiO₂[27, 28]. Here, catalysts are prepared by IWI of aqueous, anionic Fe³⁺ complexes of ethylenediaminetetraacetic acid (EDTA) onto CeO₂ supports, followed by oxidative thermal removal of the ligand. This work explores the changes in FeOx structure, redox behavior, and reactivity in NO reduction with H₂, which accompany changes in synthesis precursor (FeEDTA⁻ or Fe(NO₃)₃), alkali dopant, and surface density, all at sub-monolayer coverage. Although H₂ is not a reductant present in automotive emissions, this model system allows clearer insights into critical NO activation steps.

2. Experimental

2.1. Materials and Instruments

All reagents are obtained from Sigma-Aldrich and used as received. Catalyst precursors are synthesized under air at ambient conditions. Non-porous CeO₂ support (C.I. Kasei Co., Ltd. NanoTek powder) is dried at 120 °C under ambient air and pressure for >12h before use.

N₂ physisorption isotherms are obtained using a Micromeritics ASAP 2010 instrument. Specific surface areas were extracted from N₂ physisorption isotherms using the BET equation [29]. Before measurements, all materials are degassed 6 h at <5 mTorr and 120 °C to release absorbed water.

Elemental analysis is performed using a Varian MPX ICP-OES instrument. Samples are prepared by dissolving 50 mg of solids in 1 mL of HF and subsequently diluting to 50 mL with H₂O. Metal contents are quantified by comparison against standards of known concentration. Diffuse reflectance UV-visible (DRUV-vis) spectra are collected using a Shimadzu 3600 UV-visible-NIR spectrometer with a Harrick Praying Mantis diffuse reflection attachment. Polytetrafluoroethylene (PTFE) is used as the baseline standard and diluent. All materials are mixed with five mass equivalents of PTFE and thoroughly ground with mortar and pestle before analysis. The resulting diffuse reflectance spectra are converted to pseudo-absorption using the Kubelka-Munk transform [30]. Solution UV-vis spectra are acquired with a Shimadzu 3600 UV-visible-NIR spectrometer using a standard 1 cm pathlength quartz cell. Thermogravimetric analyses (TGA) are performed using a TA Instruments Q500 thermogravimetric analyzer

fitted with an evolved gas analysis furnace. For combustion analysis, materials are heated in 100 sccm 90% O₂ and 10% He with a temperature program of 10 °C min⁻¹ to 800 °C.

2.2. *NaFeEDTA and NH₄FeEDTA Synthesis*

The preparation of sodium Fe(III) ethylenediaminetetraacetate (NaFeEDTA) and ammonium Fe(III) ethylenediaminetetraacetate (NH₄FeEDTA) is based on that by Meier and Heinemann [31]. H₄EDTA (10 mmol) and Fe(NO₃)₃·9H₂O (10 mmol) are mixed with 25 mL of H₂O (>18 mΩ) in a 100 mL two-neck round-bottom flask. The mixture is then heated to 60 °C under ambient air while stirring until a solution forms.

To form NaFeEDTA, four equivalents of NaHCO₃ (40 mmol) are slowly added to fully deprotonate the H₄EDTA ligand, and the desired product precipitates out of solution upon cooling to ambient temperature. The resulting yellow solid is separated by filtration, washed with 5 mL of H₂O at 0 °C to remove NaNO₃ impurities, and with 15 mL of acetone to remove excess H₂O. Finally, the yellow solid is dried under dynamic vacuum (20 mTorr) for 12 h. TGA of the dry material between 150 °C and 550 °C showed a mass loss due to combustion corresponding to 98 % purity according to the ratio of organic to inorganic components.

To form NH₄FeEDTA, four equivalents of NH₄HCO₃ (40 mmol) are used to deprotonate the H₄EDTA ligand. The solution is reduced to ~5 mL by rotary evaporation and stored at -20 °C overnight. The resulting crystals are separated by filtration, washed with acetone, and dried under dynamic vacuum (20 mTorr) for 12 h. TGA of the dry material between 200 °C and 550 °C showed a mass loss due to combustion corresponding to 99.3% purity according to the ratio of organic to inorganic components.

2.3. Support modification

The support, non-porous CeO₂ (C.I. Kasei Co., Ltd. NanoTek powder) with surface area of 101 m² g⁻¹, is modified by incipient wetness impregnation (IWI) with aqueous solutions of NaHCO₃ (0.1 to 0.6 M). The incipient wetness volume required to wet the support is approximated by the total uptake volume determined by N₂ physisorption of neat CeO₂. Following impregnation, the supports are dried in partially covered containers under ambient conditions for 24 h and then heated to 120 °C for 12 h to create Na/CeO₂. TGA of the dry materials show no evidence of residual carbonates, combustible materials, or volatile groups on the surface. N₂ physisorption of the dry materials showed changes in surface area lower than 10% and a decrease in uptake volume of ~30% (Supporting Information Table S1).

2.4. Catalyst Preparation

Iron is deposited on neat and alkali-modified CeO₂ by IWI with aqueous solutions of NaFeEDTA (0.1– 0.3 M), NH₄FeEDTA (0.1 – 0.2 M), and Fe(NO₃)₃ (0.2 – 0.6 M). In all cases where Na is present in the final catalyst, Fe and Na are present in equimolar amounts. No evidence of dimeric FeEDTA complexes—with a characteristic UV-visible peak at 475 nm—is observed in the impregnation solutions [32]. Following impregnation, materials are dried for 24 h in partially covered containers under ambient conditions and for 12 h under dynamic vacuum (~20 mTorr). The aqueous solubility of NaFeEDTA (~0.3 M) limits single impregnations on CeO₂ (surface area = 101 m² g⁻¹, incipient wetness volume = 275 uL g⁻¹) to a maximum loading of approximately 0.6 Fe nm⁻². To surpass this limit, the impregnation and drying cycle is repeated multiple times.

The dry materials undergo oxidative heat treatment under static ambient air from room temperature to 550°C at a ramp rate of 10°C min⁻¹ after which point they are generically referred to as FeOx-Na/CeO₂. Fe surface densities vary in the range 0.2 to 1.5 Fe nm⁻² (Table 1), as calculated from ligand combustion by TGA and confirmed by digestion and ICP-AES.

2.5. *Temperature Programmed Reduction*

Temperature-programmed reduction (TPR) experiments are performed in a TA Instruments Q500 TGA fitted with a Pfeiffer ThermoStar Q200 process mass spectrometer. As-prepared materials are pretreated in 100 sccm 90% O₂ and 10% He following a temperature program of 10 °C min⁻¹ to 550 °C and subsequent 15 minute temperature hold. The pretreated materials are cooled to ambient temperature in 100 sccm He, then heated again at 10 °C min⁻¹ to 550 °C in 100 sccm 4.5 % H₂, 4.5 % Ar, balance He. The evolved H₂O signal, m/z = 18, is normalized by the constant flow of Ar, m/z = 40, and calibrated against the reduction of known amounts of CuO to metallic Cu under the same conditions.

Selected samples (marked *r* in Table 1) were subjected to a second oxidation and reduction cycle. After the first TPR experiment, samples are cooled to near ambient temperature in 100 sccm He, before undergoing the next cycle of oxidation, cooling under inert, and reduction.

2.6. *In situ X-ray absorption spectroscopy during H₂-TPR*

X-ray absorption near edge structure (XANES) analysis was performed at the bending magnet D beamline of the Dupont-Northwestern-Dow Collaborative Access Team (DND-CAT), in Sector 5 of the Advanced Photon Source at Argonne National

Laboratory. Incident and transmitted intensities were measured with Canberra ionization chambers. Beam energies were calibrated against Fe metal foil measured in transmittance and its K-edge was set to 7112 eV. FeO and Fe₂O₃ standards were brushed on Capton tape and their spectra were also measured in transmittance.

Supported Fe materials were pressed into 50 mg pellets 2.5 cm in diameter. Single pellets were mounted on a stainless steel heated cell designed for transversal gas flow and sealed with a Be back window and Capton front window. To ensure pellets remained against the front Capton sheet, the space between windows was filled with a loose bed of quartz wool. Due to the low Fe content of the pellets, spectra were measured as fluorescence intensity using a four-channel SII Vortex-ME4 detector. Samples were mounted at incident angle $\theta = 45^\circ$ with respect to the beam and detector, which were perpendicular to one another. Before starting the temperature program, spectra of the pellets loaded in the sample holder were compared to those of the corresponding powder materials brushed on Capton tape and measured also as fluorescence intensity.

Once mounted, pellets were subjected to transversal flow of 50 sccm 3.5 % H₂ and balance He. The heated flow cell was held at ambient temperature, 150 °C, 250 °C, 340 °C, and 430 °C for two hours each while spectra were collected. Between holds, the temperature was ramped at $\sim 10^\circ\text{C min}^{-1}$. Note that these are true sample temperatures.

2.7. Catalytic Reactions

NO reduction by H₂ was performed at atmospheric pressure in a quartz U-tube reactor (OD $\frac{1}{4}$ ", ID $\frac{1}{8}$ "). Beds composed of 25 mg of catalyst diluted in 0.50 g of non-porous quartz sand were packed in down flow between plugs of quartz wool. Before

mixing, the catalyst was pressed into pellets, lightly crushed, and sieved to 40-100 mesh size—similar to the quartz diluent. A thermocouple placed against the top of the catalyst bed was used to monitor and record temperature, which was controlled using a J-KEM 4700 safety temperature controller connected to a Applied Test Systems upright tube furnace (ID 2.5”). The thermocouple and quartz diluents showed no catalytic activity in control experiments.

The reactor inlet was connected to a gas manifold delivering 50 sccm (standard cm³ per minute) of 3.3 % NO, 3.3 % H₂, 3.3 % Ar, and balance He, corresponding to a gas hourly space velocity of approximately 10⁴ h⁻¹ for the total loading of catalyst and diluent given above. The outlet was connected to a Pfeiffer Thermostar Q200 process mass selective detector measuring reactant and product concentrations. The MSD signal corresponding to Ar (m/z = 40) was used as an internal standard by which all other signals were normalized. MSD signals corresponding to NO (m/z = 30) and N₂ (m/z = 28) were calibrated against 50 sccm flows with concentrations of NO and N₂ between 1% and 5%, which were prepared by dilution of 5% NO/He and 5% N₂/He mixtures in pure He. To avoid signal crossover with H₂O, m/z = 16 was used to track NH₃ evolution. This signal was calibrated against the thermal decomposition at 42 °C of known amounts of NH₄HCO₃ in a 50 sccm flow of He.

Packed reactors were fed 50 sccm of the reaction mixtures, heated at 10 °C min⁻¹ to 150 °C, 250 °C, 350 °C, 450 °C, and 550 °C, and held at each temperature for 1 h. Complete disappearance of signals corresponding to atmospheric N₂, O₂, H₂O, and CO₂, as well as surface H₂O, was observed within 20 minutes at 150 °C. Additionally, because

no reaction was observed at 150 °C, the gas concentrations of the final 30 minutes at this temperature were used as the baseline.

3. Results and Discussion

3.1. Diffuse reflectance UV-visible spectrophotometry

For both synthesis methods, powder X-ray diffraction (XRD) shows no indication of crystalline FeOx phases. Because even the highest surface loading is only a fraction of a statistical monolayer, typically assumed to form at 4-6 atoms.nm⁻², the formation of crystallites would not be expected. Thus, diffuse reflectance UV-visible (DRUV-vis) spectrophotometry was used to examine the dispersion of Fe surface species on the FeOx-Na/CeO₂ materials. For inert oxide supports, isolated Fe³⁺ ions are expected to show oxygen-to-metal charge transfer bands below 300 nm, two-dimensional oligomers between 300 nm and 500 nm, and larger aggregates above 500 nm [15, 18, 24, 33, 34]. For the materials in this study, bands that could correspond to isolated ions are obscured by the strong absorption of CeO₂ below 350 nm. For redox active supports such as CeO₂, red-shifted absorption bands could also correspond, in principle, to metal-to-metal charge transfer between Fe and Ce.

Figure 1 shows FeOx-Na/CeO₂ prepared from NaFeEDTA and Fe(NO₃)₃. Both sets of materials show absorption tails extending beyond that of CeO₂ and growing with increasing Fe loading. Supporting Information Figure S1 shows a corresponding increase in red color with increasing loading. For all materials, pseudoabsorption intensity beyond that of CeO₂ is predominantly in the range of 300-500 nm, suggesting a significant population of two-dimensional oligomers or small clusters. At the highest loadings of the EDTA-derived materials, an additional feature appears at higher wavelengths, likely

associated with larger, but still non-crystalline oxide clusters. For a given loading, there are no significant differences in color between samples made by the two methods. (Supporting Information Figure S1) Studies by others have observed that supports with surface vacancies such as CeO₂ tend to incorporate Fe³⁺ and other cations into vacant sites [16][35]. Therefore, the negative charge and large size of the FeEDTA complex may alter the distribution of how the Fe³⁺ ions interact with the surface vacancies and reducible sites on CeO₂, as compared to Fe(NO₃)₃. This distribution is quantified by examining their reducibility below.

3.2. Temperature programmed reduction

Dispersion and agglomeration of supported transition metal oxides are related to redox properties which can be probed by TPR. Monomeric Fe³⁺ structures interacting strongly with inert oxide supports are expected to reduce at higher temperature than agglomerates more closely resembling bulk oxides [18]. Specifically, isolated Fe³⁺ ions on an irreducible support like SiO₂ are expected to reduce in H₂ between 600 °C and 700 °C, [27, 28] while 2D sheets or clusters and 3D aggregates reduce around 500 °C and 400 °C, respectively [21, 34]. These generalizations do not necessarily hold on redox-active or zeolite supports. Regardless of their assignment, the highest temperature reduction features are not accessible here due to bulk reduction of CeO₂ starting at ~600 °C. Such sites are also not relevant to the catalytic reactions described here, which occur at 550 °C and below.

3.2.1. General Behavior

Figure 2A shows the TPR profiles of FeOx-Na/CeO₂ prepared from NaFeEDTA on CeO₂ and that of Na/CeO₂. The total H₂O evolved from these materials during reduction

between 150—550 °C (Figure 3) increases linearly with Fe loading. The non-zero intercept matches the H₂O evolved during the reduction of neat CeO₂ in the same temperature range. While both CeO₂ and FeOx reduce in this temperature range, the excess evolved H₂O – that of FeOx-Na/CeO₂ less that of Na/CeO₂ – is directly proportional to the Fe content. This proportionality shows that the fractional reduction is independent of surface density within this range of loadings. The slope of the linear fit in Figure 3, 0.23 mol excess H₂O per mol Fe, corresponds to an average reduction from Fe(III) to Fe(II) of 45 ± 6 %. Keep in mind that the parallel reduction of the CeO₂ surface is also occurring, but not factored into these values. As a corollary, approximately half the total Fe is likely present as highly dispersed surface or near-surface Fe species that do not undergo redox transitions within the explored temperature range.

Materials prepared from Fe(NO₃)₃ show similar TPR profiles as those derived from FeEDTA (Figure 2B), except that the excess H₂O evolved during reduction (Figure 3) corresponds to an average reduction from Fe(III) to Fe(II) of 23 ± 6 %. The lower extent of reduction relative to materials prepared from FeEDTA indicates that the nitrate precursor results in different interactions with the ceria support, which creates sites unreducible in this temperature range. This is in agreement with our hypothesis that both precursors yield oligomers and small clusters of FeOx, but differently distribute Fe³⁺ ions amongst vacancies, reducible sites, and other regions on the CeO₂ surface, with EDTA increasing the number of reducible sites.

3.2.2. *Fe Speciation*

TPR profiles can be deconvoluted into four Gaussian curves here ascribed to separate reduction events (example in Figure 2C, 2D). It is clear from TPR profiles of Na/CeO₂

(Figure 2A and 2B, gray lines) that reduction events centered on 350 °C and 500 °C correspond to the surface reduction of the support, in agreement with observations reported in the literature [15]. Thus, the ceria surface is reducing in parallel with the reduction of the FeOx sites.

Materials prepared from FeEDTA display two additional features; one at 400 °C present in all materials and another at 300 °C which emerges at loadings above 0.9 Fe nm⁻² (Figure 2C). The low reduction temperatures and the lack of crystalline FeOx is consistent with these features being assigned as different types of two-dimensional FeOx oligomers or small clusters well dispersed on the surface. Materials prepared from Fe(NO₃)₃ show the reduction event at 400 °C only (Figure 2D), assigned as a single type of FeOx cluster, again to be consistent with the DRUV-vis. The remaining FeOx (~55% for EDTA-derived materials and ~75% for nitrate-derived materials) may be present as several different types of non-crystalline FeOx that are not reducible over this temperature range.

3.2.3. $Fe^{3+}—Fe^{2+}$ redox cycle

As described in the experimental section, selected materials (marked *r* in Table 1) underwent a second oxidation to 550 °C and TPR after the first TPR experiment. The total area of the reduction features at 350 °C and 500 °C corresponding to CeO₂ are unaffected, indicating the support reduces to the same extent during the second cycle. However, at the highest Na loadings, the CeO₂ reduction feature at 350 °C broadens out on a second reduction cycle without a change in total integrated area (Supporting Information Figure S2). The phenomenon is attributed to the higher alkali loading

combined with the repeated heating cycles. The small drop in surface area at higher Na loadings (Supporting Information Table S1) also suggests structural alterations of the support as consequence of the alkali and repeated temperature cycling.

Materials with loadings of 0.9 Fe nm^{-2} or below display only one feature correlated to FeOx (centered at 400°C) which changes minimally between cycles (Supporting Information Figure S3), indicating these species are capable of reversible $\text{Fe}^{3+} \text{—} \text{Fe}^{2+}$ redox cycles relevant for catalysis. For materials prepared with FeEDTA and loadings of 1.2 and 1.5 Fe nm^{-2} such as shown in Figure 2C, the unique feature at 300°C is absent on the second TPR (Supporting Information Figure S3), and the reduction event near 400°C appears at slightly lower temperature and decreases substantially in total area (by 24% and 42% for 1.2 and 1.5 Fe nm^{-2} , respectively) in the second TPR. The net result is that the fraction of Fe atoms undergoing reversible $\text{Fe}^{3+} \text{—} \text{Fe}^{2+}$ redox cycles decreases beyond $\sim 0.9 \text{ Fe nm}^{-2}$ (data summarized in Figure 4). Interestingly, there is no accompanying significant change in the DRUV-vis spectra after multiple TPR cycles. Thus, we ascribe the change in reducibility to small changes in the distribution of FeOx sites and how they interact with the CeO_2 surface, rather than wholesale changes to the FeOx aggregates themselves. The particular reducibility limit of $\sim 0.9 \text{ nm}^{-2}$ may suggest an intrinsic feature related the reducible surface sites on this ceria support. A third oxidation-reduction cycle of the materials with 1.2 Fe nm^{-2} (Supporting Information Figure S4) shows the same profile as the second TPR, indicating that the surface species stabilize after the first redox cycle.

3.3. X-ray absorption spectroscopy

Figure 5 shows pre-edge and XANES spectra of FeOx-Na/CeO₂ materials during reduction with dilute H₂ between ambient temperature and 430 °C. The spectra correspond to materials (marked *x* in Table 1) prepared from NaFeEDTA on CeO₂ (Figure 6A-6C) and Fe(NO₃)₃ on Na-modified CeO₂ (Figure 5D). All the materials tested show pre-edge features more intense than those of the bulk oxide standards, indicating undercoordinated FeOx species [36]. For materials derived from NaFeEDTA on CeO₂ (Figure 5A-5C), the intensity of the pre-edge band decreases with increasing Fe surface density, which is consistent with the shift in DRUV-vis spectra, and suggesting increasing Fe-O coordination numbers with increasing loading, which could indicate larger clusters or more thorough incorporation into the ceria lattice.

For all materials, the absorption edge remains between that of Fe³⁺ and Fe²⁺ at all temperatures. This indicates the presence of the Fe²⁺ oxidation states even after the original calcination and a return to ambient temperature. To determine the relative concentration of the two oxidation states, the spectra of the supported materials are fitted to linear interpolations of those of bulk FeO and Fe₂O₃ in the near-edge region between 7117 eV and 7124 eV—the range where the absorption edges of Fe²⁺ and Fe³⁺ appear. This method reliably predicts the fractions of Fe³⁺ and Fe²⁺ in experimentally-acquired spectra of mixed valence bulk Fe₃O₄. In addition, samples of calcined FeOx on SiO₂ made by the same methods show 100% Fe³⁺ oxidation state, as expected.

For materials prepared from NaFeEDTA on CeO₂, the change in absorption edge between ambient temperature and 430 °C corresponds to 28%, 39%, and 37% reduction

from Fe^{3+} to Fe^{2+} for Fe loadings 0.6 Fe nm^{-2} , 0.9 Fe nm^{-2} , and 1.5 Fe nm^{-2} . According to TPR experiments, average Fe^{3+} to Fe^{2+} reduction up to 430°C yields partial Fe^{3+} to Fe^{2+} reductions of 32%, 37%, and 39%, respectively; the two experiments are in remarkable agreement. For the material prepared from $\text{Fe}(\text{NO}_3)_3$ on Na/CeO_2 , the change in absorption edge between ambient temperature and 430°C corresponds to approximately 9% of the Fe transition from Fe^{3+} to Fe^{2+} , while TPR experiments show a slightly higher value of 17% reduction of the FeOx in this material up to 430°C . Given the lower extent of reduction, the values remain in good agreement.

Overall, X-ray absorption and TPR experiments are in good quantitative and qualitative agreement, and both indicate that NaFeEDTA on CeO_2 produces a larger fraction of reducible Fe species than $\text{Fe}(\text{NO}_3)_3$ on Na-modified CeO_2 . This is made clear in Figure 6, which shows the Fe^{3+} fraction determined by XANES as function of temperature for two materials with similar surface densities but different precursors: 0.9 Fe nm^{-2} prepared from NaFeEDTA on CeO_2 and 1.0 Fe nm^{-2} prepared from $\text{Fe}(\text{NO}_3)_3$ on Na/CeO_2 .

Recalling that the starting Fe oxidation state was always less than $3+$, the presence of Fe^{2+} even before reduction suggests that a fraction of the CeO_2 was initially present as Ce(III) and reduced Fe^{3+} to Fe^{2+} during the initial synthesis. The density of permanently-reduced Fe^{2+} species remains in the narrow range of $0.11 \pm 0.02 \text{ Fe nm}^{-2}$ for all materials prepared from NaFeEDTA and 0.16 Fe nm^{-2} for those derived from $\text{Fe}(\text{NO}_3)_3$.

Combining the TPR and XANES data generates a picture of the FeOx speciation from the two precursors. Taking 0.6 Fe nm^{-2} as an example, the EDTA precursor leads to $\sim 0.1 \text{ Fe nm}^{-2}$ as permanently-reduced Fe^{2+} , $\sim 0.3 \text{ Fe nm}^{-2}$ of Fe^{3+} species reducible at ~ 400

°C, and $\sim 0.2 \text{ Fe nm}^{-2}$ as any one of a number of redox-inactive Fe^{3+} species. The nitrate precursor, in contrast, leads to fewer of the redox-active sites ($\sim 0.15 \text{ Fe nm}^{-2}$), and more of the permanently-reduced and unreducible sites (~ 0.15 and $\sim 0.3 \text{ Fe nm}^{-2}$, respectively).

3.4. Catalytic Reduction of NO by H_2

FeOx-CeO_2 and FeOx-Na/CeO_2 materials were tested as catalysts in the reduction of NO by stoichiometric H_2 between 150 °C and 550 °C. NO conversions range from 14% to 63%, with values increasing monotonically with temperature and Fe loading, as expected. Direct decomposition of NO in the absence of H_2 over the oxidized materials is not observed in this temperature range. Using only N_2 and NH_3 as products, the N balance—defined as moles of N in products over moles of consumed NO—is between 75 % and 105 % for 350 °C and above. The lower values are observed at lower temperatures and conversions, and the discrepancy is attributed to limits in instrumental precision.

Figure 7 shows the rate of consumption of NO, in $\mu\text{mol g}_{\text{cat}}^{-1} \text{ s}^{-1}$, of a representative catalyst (0.6 Fe nm^{-2} from NaFeEDTA on CeO_2) and a related Na-modified support (0.5 Na nm^{-2} on CeO_2) at four different temperatures. Na/ CeO_2 and CeO_2 display moderate baseline activity that is largely independent of alkali loading. Supports show selectivity towards N_2 between 45-65% while Fe containing materials are 85-95% selective towards N_2 . Interestingly, Fe containing materials do not exceed the baseline activity of the support below 350 °C. Recall that 350 °C marks the onset of reduction of Fe species capable of Fe^{3+} — Fe^{2+} cycles. This suggests a relation between those Fe surface structures and activity of these FeOx-CeO_2 materials in NO reduction.

Fe-containing materials show the greatest difference relative to the support at 450 °C (Figure 7). Hence, reaction rates at that temperature will be used when discussing the effects of Fe surface density and precursor.

3.4.1. *Catalyst preparation vs. activity*

First, catalysts were tested for the role of the Na promoter. At a representative surface density of 0.5 Fe.nm⁻² and 450°C, NaFeEDTA/CeO₂ outperforms NH₄FeEDTA/CeO₂ (material 8, Table 1, no alkali) by >40% (Figure 8). Considering that Na has no effect on the background rate of reaction by the support, Na promotion nearly doubles the Fe-associated contribution to the NO reduction rate. Different methods of addition for Na and FeEDTA⁻ (NaFeEDTA on CeO₂ vs. NH₄FeEDTA on Na/CeO₂, e.g. material 9 in Table 1) give identical rates within uncertainty. For all loadings, the NaFeEDTA precursor is seen to outperform the nitrate precursor, but particularly at lower loadings. From these comparisons, both the chelating ligand and the alkali dopant are necessary for the highest performance. Beyond these internal comparisons, the reduction of NO with H₂ at 450°C by these FeOx-Na/CeO₂ materials compares favorably to that of a Pd/Al₂O₃ standard (Figure 8): 1.0 wt% FeOx-CeO₂ from NaFeEDTA shows a rate of 26 μmol (g cat)⁻¹ s⁻¹, while 1.0 Pd wt% Pd/Al₂O₃ shows a rate of 24 μmol (g cat)⁻¹ s⁻¹.

Finally, for heat-treated materials prepared from NaFeEDTA on CeO₂, the integrated NO consumption rate at 450 °C increases linearly with Fe content up to 0.9 Fe nm⁻², where it enters a plateau in activity (Figure 8). If one recalls, 0.9 Fe nm⁻² also marks the onset of a plateau in the surface density of species capable of Fe³⁺—Fe²⁺ redox cycling (Figure 4). Based on the common trend, the activity of these materials is assigned to redox-cycling Fe species. A similar assignment can be made for materials prepared from

$\text{Fe}(\text{NO}_3)_3$ on Na/CeO_2 , but the relation here is simpler because the population of redox-active Fe and absolute NO reduction rate are both linear with respect to Fe loading.

Figure 9 plots the observed integrated rates for all the FeOx-Na/CeO_2 materials, regardless of precursor, against the number of redox-cycling Fe. While the rate data were not acquired under differential conditions, these rates are independent of P_{H_2} and P_{NO} between 0.01 and 0.03 atm (Supporting Information Figure S5), covering the range of conversions (14-63%) exhibited by these catalysts. In Figure 9, all materials collapse to a single trendline. Materials derived from $\text{Fe}(\text{NO}_3)_3$ give lower levels of redox-active Fe and correspondingly lower rates. The plateau in both redox-active Fe and NO reduction rate for NaFeEDTA -derived materials is seen as a cluster of points at the upper end of the plot. The single trendline for different redox-capable Fe populations, present in different surface densities and prepared by different methods, supports their assignment as the active phase.

4. Conclusions

This work illustrates a straightforward methodology to create materials for the reduction of NO to N_2 with H_2 based on Fe oxides loaded on CeO_2 instead of precious metals. Alkali cations, added before or simultaneously to the Fe precursor, appear to serve as structural promoters, increasing observed rates beyond that of FeOx-CeO_2 alone. Although the exact role of the promoter remains under investigation, it may act by titrating the surface vacancies that would otherwise incorporate Fe cations and form inactive species. These materials containing under-coordinated Fe surface structures on Na/CeO_2 show NO reduction rates, per mass of catalyst, comparable to those of similar

loadings of Pd on Al₂O₃. The activity of these materials in the reduction of NO with H₂ is correlated to a subset of the FeOx oligomers present on the surface, as determined from DRUV-vis, TPR, and XANES. These active structures are capable of undergoing reversible Fe³⁺–Fe²⁺ redox cycles under reaction conditions, as demonstrated from repeated TPR cycles.

These redox-active surface structures are most selectively formed by incipient wetness impregnation of CeO₂ with aqueous NaFeEDTA—a bulky, negatively charged complex. The EDTA ligand gives more of the redox-active FeOx and less of the permanently-reduced and the redox-inactive FeOx species, as compared to a more typical Fe(NO₃)₃ precursor. For all materials prepared from NaFeEDTA on CeO₂ and Fe(NO₃)₃-on Na/CeO₂, rates collapse to a single trendline when plotted against the amount of FeOx undergoing reversible Fe³⁺—Fe²⁺ cycles. This correlation, in spite of the difference in precursor, supports the hypothesis that this particular sub-population of surface structures is responsible of the activity of these materials. The identity of these FeOx sites is currently under scrutiny by other techniques. More rigorous kinetic evaluation with reductants more relevant to real tailpipe emissions (e.g. CO and hydrocarbons) is also underway and will be reported elsewhere. Finally, further optimization of the promoter type, promoter amount, and the Fe precursor identity offers opportunities for additional enhancement of catalytic reactivity.

5. Acknowledgements

JMN and DPC acknowledge the support of Toyota Motor Company, and thank Pria Young and Boone Thompson for helpful discussions. Portions of this work were performed with the invaluable help of Dr. Qing Ma at the DuPont-Northwestern-Dow

Collaborative Access Team (DND-CAT) located at Sector 5 of the Advanced Photon Source (APS). DND-CAT is supported by E.I. DuPont de Nemours & Co., The Dow Chemical Company, and Northwestern University. Use of APS, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under contract No. DE-AC02-06CH11357. JMN and TRE acknowledge the DOE Office of Basic Sciences grant SC-0006718, which supported materials characterization activities.

Figure Captions

Figure 1. DRUV-vis spectra of FeOx-Na/CeO₂ prepared from (A) NaFeEDTA on CeO₂ and (B) Fe(NO₃)₃ on Na/CeO₂. The gray line corresponds to Na-doped CeO₂ with a surface loading of 1.0 Na nm⁻².

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Figure 5. Pre-edge and XANES spectra collected during reduction in H₂ flow from ambient temperature to 430 °C for FeOx-Na/CeO₂ from A) NaFeEDTA at 1.5 Fe nm⁻², B) NaFeEDTA at 0.9 Fe nm⁻², C) NaFeEDTA at 0.6 Fe nm⁻², and D) Fe(NO₃)₃ at 1.0 Fe nm⁻². Reference spectra of Fe₂O₃ and FeO are given in grey.

Figure 6. Fraction of Fe³⁺ present as a function of temperature for 0.9 and 1.0 Fe nm⁻² materials prepared from NaFeEDTA on CeO₂ and Fe(NO₃)₃ on Na/CeO₂, respectively. Note the nearly constant Fe³⁺ fraction for the Fe(NO₃)₃-derived material.

Figure 7. Rates of NO consumption towards NH₃ and N₂ for Na/CeO₂ (0.5 Na nm⁻²) and FeOx-Na/CeO₂ derived from NaFeEDTA on CeO₂ (0.6 Fe nm⁻²) at different temperatures. Differences in activity between support and catalysts are greatest at 450 °C. Fe-containing materials are more selective towards reduction of NO to N₂ relative to the support.

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Table 1. Characteristics of FeOx-CeO₂ materials

Material #	Precursor	Support	Fe Loading ^a			Notes
			wt %	μmol g ⁻¹	at. nm ⁻²	
1	NaFeEDTA	CeO ₂	0.18	32	0.19	<i>r</i>
2	NaFeEDTA	CeO ₂	0.34	60	0.36	
3	NaFeEDTA	CeO ₂	0.52	92	0.55	
4	NaFeEDTA	CeO ₂	0.53	94	0.56	<i>r, x</i>
5	NaFeEDTA	CeO ₂	0.81	145	0.87	<i>r, x</i>
6	NaFeEDTA	CeO ₂	1.16	207	1.23	<i>r</i>
7	NaFeEDTA	CeO ₂	1.38	246	1.47	<i>r, x</i>
8	NH ₄ FeEDTA	CeO ₂	0.48	86	0.51	
9	NH ₄ FeEDTA	Na/CeO ₂	0.49	87	0.52	
10	Fe(NO ₃) ₃	Na/CeO ₂	0.43	82	0.49	<i>r</i>
11	Fe(NO ₃) ₃	Na/CeO ₂	0.87	164	0.98	<i>r, x</i>
12	Fe(NO ₃) ₃	Na/CeO ₂	1.35	255	1.52	<i>r</i>

^a Loadings confirmed by ICP-OES and surface densities based on BET surface area of the neat support.

^r Material underwent multiple cycles of TPR.

^x XANES spectra in Figure 6.

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