Roles of Fe^{2+} , Fe^{3+} and Cr^{3+} Surface Sites in the Oxidation of NO on the $(\text{Fe,Cr})_3\text{O}_4(111)$ Surface Termination of an $\alpha\text{-(Fe,Cr)}_2\text{O}_3(0001)$ Mixed Oxide

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Abstract

The oxidation of NO was explored on a mixed Fe+Cr oxide surface using temperature programmed desorption (TPD). NO desorbs from $(\text{Fe,Cr})_3\text{O}_4(111)$ in two main peaks at 220 and 370 K, with a third minor peak at ~315 K. O_2 TPD shows similar behavior. The strongly and weakly bound molecules are due to adsorption at Fe^{2+} and Fe^{3+} sites, respectively, and the minor states are assigned to Cr^{3+} sites. No thermal decomposition was detected for adsorbed NO, whereas ~10% of the adsorbed O_2 dissociated at Fe^{2+} sites. NO reacts with preadsorbed O_2 to produce surface nitrate, as confirmed by isotopic labeling, which decomposes in TPD at 425 K. Atomically adsorbed O does not react with NO. Fe^{3+} and Cr^{3+} sites do not appear to participate in NO oxidation. Irradiation of adsorbed NO or $\text{NO}+\text{O}_2$ with 460 nm light results predominantly in photodesorption, which limits the extent of possible surface photoreactions.

1. Introduction

Fe-containing catalysts have become important in the selective catalytic reduction (SCR) of NO because the presence of Fe^{2+} and Fe^{3+} sites enable a variety of redox reactions for both NO and its reducing agent (typically NH_3 or a hydrocarbon).¹⁻¹⁰ The more active catalysts tend to have iron mixed into another oxide's framework (usually a zeolite), with the structural environment of the iron cation sites playing an important role in reactivity. There are still many questions regarding the roles of Fe^{2+} and Fe^{3+} sites in specific mechanistic steps of the SCR process. For example, there is uncertainty in the literature about the active forms of iron (e.g., individual cations, small oxide clusters or bulk oxide phases) for NO oxidation. Indeed, multiple

forms. The mechanism and key surface sites for NO oxidation on Fe-based catalysts are not well understood. It is generally held that NO oxidation is a key mechanistic step prior to reduction to N₂ because NO reduction is more difficult than nitrate reduction.^{4,5} Iron oxides have also received renewed attention as potential visible light photocatalysts because of the favorable overlap between their optical absorption spectra and the solar emission spectrum,¹¹⁻¹⁷ with mixed oxides containing Fe showing added potential benefits.¹⁸⁻²³ In this study, the chemical and photochemical properties of NO were explored on the mixed (Fe,Cr)₃O₄(111) surface with a focus on oxidation. The surface chemistry and photochemistry of NO have been examined on a variety of well-ordered oxide surfaces,²⁴⁻³⁷ however there are no available studies in literature on an Fe-based single crystal oxide surface. Results in this study suggest that Fe²⁺ surface sites on (Fe,Cr)₃O₄(111) are active for NO oxidation, whereas Fe³⁺ and Cr³⁺ sites bind NO but are comparatively inactive for its oxidation. Visible light irradiation does not promote (additional) NO oxidation, but actually limits the extent of thermal oxidation (under UHV conditions) by photodesorbing the reactants from the surface.

2. Experimental Section

The (Fe,Cr)₃O₄(111) surface employed in this study was obtained from a 500 Å thick α-(Fe,Cr)₂O₃(0001) film that was grown by oxygen plasma-assisted molecular beam epitaxy on an α-Al₂O₃(0001) crystal.^{23,38} Vacuum cleaning (sputtering and annealing) of a α-Fe₂O₃(0001) surface is known to give the Fe₃O₄(111) termination,³⁹⁻⁴² but this does not occur for α-Cr₂O₃(0001).⁴³ For the mixed α-(Fe,Cr)₂O₃(0001) surface, sputter/anneal treatments transformed the surface from a corundum (0001) structure into a magnetite-like (111) structure.⁴⁴ This transformation was evident in low energy electron diffraction (LEED) by a (2x2) pattern similar to that obtained from Fe₃O₄(111),⁴⁵⁻⁴⁷ in x-ray photoelectron spectroscopy (XPS) by Fe 2p spectrum consistent with Fe²⁺ (Fe 2p_{3/2} at 710.8 eV and satellite at 715.5 eV) and chemical reactivity consistent with a magnetite-like (111) surface.⁴⁴ The as-grown film possessed an Fe:Cr ratio of ~3:1, but Cr-enrichment in the sputter/annealed surface was evident in both XPS and secondary ion mass spectrometry (SIMS) by a surface cation compositional ratio of ~1.4:1.

The crystal was held against a Au-coated Ta plate that could be cooled to 40 K by a He cryostat and heated resistively to >1000 K, with the temperature monitored by a chromel-alumel thermocouple. Surface characterization with charge particle probes (such as SIMS or Auger

electron spectroscopy) was limited by the insulating nature of the sapphire substrate. The surface was routinely cleaned in UHV (chamber base pressure below 2×10^{-10} Torr) by heating to >900 K. This simple treatment gave consistent TPD spectra that suggested the same $(\text{Fe,Cr})_3\text{O}_4(111)$ surface was repeatedly achieved.

Isotopically labeled $^{15}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{18}\text{O}$ (Cambridge Isotope Laboratories) were further purified by liquid nitrogen (LN2) freeze-pump-thaw cycles and vacuum distillation. The N-isotopic purities in the $^{15}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{18}\text{O}$ sources were ~ 98 and $\sim 96\%$, respectively, however the O-isotopic purity in the $^{15}\text{N}^{18}\text{O}$ source was only $\sim 86\%$. Both nitric oxide and oxygen gases were dosed using a three-stage molecular beam system that produced a dosing spot on the surface of ~ 5 mm in diameter. Gas exposures, expressed in terms of ‘Torr-seconds’, were derived from the backing pressure entering the first stage of molecular beam doser and the dosing time. TPD experiments were conducted with a heating rate of ~ 2 K/s in a line-of-sight configuration between the sample and the entrance to the quadrupole mass spectrometer (QMS).

Photochemical measurements in this study were conducted with a 460 nm light emitting diode (LED) source (Prizmatix Ltd.). Light was delivered to the surface through a fused silica fiber optic cable. The surface area of irradiation was ~ 7 mm in diameter, which was positioned over the dosing spot (see above). The 460 nm LED output, as determined with a Si photodiode, was 256 mW ($\sim 5.9 \times 10^{17}$ photons/s). The maximum temperature rise detected during irradiation at 40 K was 2 K.

3. Results and Discussion

Results in this study are divided into four sections: the first two focusing on the individual surface chemistries of NO and O_2 on the clean surface, the next on the coadsorption of these two molecules in the context of NO oxidation, and the final on the potential of using visible light to promote NO oxidation.

3.1 ^{15}NO surface chemistry

Figure 1 presents ^{15}NO TPD spectra from various exposures of ^{15}NO (in units of Torr-s) dosed on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface at 40 K. Low exposures of ^{15}NO simultaneously populated two TPD states at ~ 230 and 385 K. The intensities in these states increased at roughly the same rates as a function of increasing ^{15}NO exposure, with each peak shifting to lower temperature (to

220 and 370 K, respectively) with increasing exposure up to ~13 Torr-s. A third ^{15}NO adsorption state was also detected between these features at ~315 K (see below). The TPD peak area ratio in the 220 and 370 K states after a 13.5 Torr-s exposure was ~1:1.8 (using a delineation temperature of 270 K).

The simultaneous filling of two adsorption/desorption states is atypical in TPD because stronger binding sites tend to be populated preferentially in systems where the incident molecule is able to sample the surface via diffusion either upon adsorption or during the TPD experiment. In the case of ^{15}NO on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface, it would appear that incident ^{15}NO molecules were unable to sample available adsorption sites either during adsorption or in the subsequent TPD. The simultaneous filling of the 220 and 370 K ^{15}NO TPD states could result from the inability of NO to hop between adsorption sites. Alternatively, adjacent terraces on the surface could have different termination structures. Magnetite-like (111) surfaces can be terminated at three different cation layers.^{45,47,48} There are two types of coordination environments (octahedral and tetrahedral) for the cation sites, along with two different cation valences (2+ and 3+) and two different elements available (Fe and Cr). These possibilities offer many potential surface cation sites that could be filled simultaneously if there were limited communication of molecules between terraces.

Higher exposures of ^{15}NO (>13 Torr-s) saturated the 220 and 370 K TPD states, and populated lower temperature desorption states at ~110 and 140 K. Desorption of nitric oxide in this temperature range has previously been assigned to physisorbed and/or dimerized NO.²⁸ A sharp desorption feature appeared at 65 K with an exposure of 37.8 Torr-s. This was assigned to desorption of physisorbed ^{15}NO and not due multilayer ^{15}NO (which desorbed at ~40 K).

The adsorption sites for ^{15}NO associated with the 220 and 370 K TPD states have been assigned to desorption from Fe^{3+} and Fe^{2+} sites, respectively, with the weak feature at ~315 K assigned to Cr^{3+} sites.⁴⁴ These assignments were made based on comparisons of the adsorption/desorption properties of various probe molecules, correlated with literature results for those molecules on model iron and chromium oxide surfaces. The decisive observation for assigning the ^{15}NO adsorption sites came from the impact of O_2 on ^{15}NO adsorption, discussed below. Molecular oxygen does not bind strongly to Fe^{3+} sites on iron oxide single crystal surfaces, but does to Fe^{2+} sites.⁴⁹ As will be shown, preadsorbed O_2 blocks access of ^{15}NO to the 370 K state, but not the 220 K state, leading to the conclusion that the 370 K ^{15}NO TPD state is

associated with Fe^{2+} surface sites. The relative adsorption strengths of NO at Fe^{2+} and Fe^{3+} sites remains controversial, and dependent on the coordination environment of the iron cations. In this case, the coordination environments of Fe^{2+} , Fe^{3+} or Cr^{3+} sites in the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface are not known for certain.

The TPD uptake for the data in Figure 1 (see inset) followed a straight line reflective of reversible adsorption-desorption behavior without thermal decomposition. No decomposition products (e.g., $^{15}\text{N}_2$ or $^{15}\text{N}_2\text{O}$) were detected in TPD. The ^{15}NO sticking probability on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface at 40 K was estimated in Figure 2 (using the King & Wells approach⁵⁰) at ~ 0.72 for the entire exposure range explored in Figure 1. The sticking probability showed no change as the 220 and 370 K ^{15}NO TPD states filled. The ^{15}NO sticking probability decreased slightly (i.e., the ^{15}NO QMS signal increased) as the 65 K peak saturated and multilayer ^{15}NO was formed. An initial sticking probability of ~ 0.7 for ^{15}NO on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface at 40 K indicates that roughly 3 in 10 molecular collisions between ^{15}NO and the surface did not trap ^{15}NO as an adsorbate despite the fact that adsorption sites were available in abundance. Interestingly, McClure et al.⁵¹ also found that NO exhibited a constant, non-unity sticking probability of ~ 0.7 at 85 K on an oxygen-covered Au(111) surface. These two examples of non-unity initial sticking probabilities of NO at low adsorption temperatures is suggestive in both cases that NO is sensitive to the electronically corrugation of an oxide surface. In other words, incident collisions between NO molecules and surface oxygen sites lead to reflection of NO rather than adsorption. The observation of an initial non-unity sticking probability in this case suggests that the simultaneous filling of the 220 and 370 K states in Figure 1 could be the result of simple ballistic hit-and-stick properties of NO and not (necessarily) due to the presence of multiple oxide surface domains.

3.2 O_2 surface chemistry

The TPD behavior of O_2 on $(\text{Fe,Cr})_3\text{O}_4(111)$, shown in Figure 3, has similarities with that of ^{15}NO (Figure 1). (The surface was heated to >900 K after each O_2 TPD experiment in Figure 3. See below for significance of this heat treatment.) As was seen for ^{15}NO , increasing O_2 exposures populate two TPD states (100 and 235 K) simultaneously, with their respective peak maxima shifting down in temperature slightly with increasing O_2 exposure. The ratio of O_2 in these two peaks at saturation was approximately the same ($\sim 1:2$) as that seen for ^{15}NO in Figure

1, although the presence of a physisorbed O₂ TPD peak at 60 K at higher exposures made it difficult to accurately estimate the O₂ peak area in the 100 K state. An additional similarity was found in the presence of a weak O₂ peak at 155 K residing between the two main O₂ peaks at 100 and 235 K. O₂ and NO both possess positive electron affinities,⁵² with the value for O₂ being slightly greater, suggesting that both molecules should compete for Fe²⁺ and Fe³⁺ sites similarly. Comparison of Figure 1 and 3 show that the adsorption behaviors of O₂ and ¹⁵NO as a function of exposure do resemble each other. It is therefore reasonable to propose that the O₂ adsorption sites for the 100, 155 and 235 K TPD states in Figure 3 could be the same as those ¹⁵NO at 220, ~315 and 370 K in Figure 1, respectively.

In contrast to the similarities between the TPD behaviors of ¹⁵NO and O₂ on the (Fe,Cr)₃O₄(111) surface shown in Figures 1 and 3, data in Figure 4 indicates a noteworthy difference. As mentioned above, no evidence was found in TPD for ¹⁵NO decomposition on the (Fe,Cr)₃O₄(111) surface. Figure 4 shows that repetitive O₂ TPD runs, where the maximum temperature in each case was limited to ~520 K, resulted in depopulation of the 235 K O₂ TPD state. The amount of O₂ desorbing in the 230 K TPD state progressively decreased with each O₂ TPD cycle. The signal strength in the 100 K state also showed small decreases with repetition of the O₂ TPD, but to a lesser extent seen for the 230 K TPD state. The inset shows a plot of the TPD peak area in the 230 K state as a function of the TPD cycle number. The loss of O₂ TPD peak area was greatest between the 1st and 2nd cycles (at ~22%), lessening with each subsequent experiment. These data do not provide insight into how dissociated O₂ blocks adsorption of subsequent dosed O₂ molecules. It could be that two O₂ adsorption sites were blocked by each dissociating O₂ molecule or that only one site was affected. The cumulative amount lost after the 6th cycle was ~43%. This behavior clearly indicates that a portion of the adsorbed O₂ adlayer decomposed (to O adatoms) and blocked surface sites used by O₂. These sites could be regenerated by heating the surface to 900 K, as shown by the dashed trace in Figure 4 and the 230 K O₂ peak area shown in the 7th cycle of the inset. Heating the surface above 900 K apparently restored the surface, allowing maximum adsorption capacity of O₂, as seen in the data of Figure 3.

3.3 Coadsorption of ^{15}NO and O_2

The ability of O_2 to thermally dissociate on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface opens the possibility that O_2 can oxidized coadsorbates on this surface. This section examines the possibility for such oxidation reactions in the coadsorption of ^{15}NO and O_2 . The first combination of these molecules explored was ^{15}NO adsorbed on a surface with the 230 K O_2 TPD state (Figure 5). The latter was accomplished by adsorbing a saturation coverage of O_2 at 40 K, followed by preheating the surface to 120 K to desorb all but the 230 K state, followed by ^{15}NO exposure at 40 K. (The ^{15}NO exposure employed was ~ 13.6 Torr-s, which was sufficient to saturate the 220 and 370 K ^{15}NO states without excess ^{15}NO .) The gray traces in Figure 5 correspond to the relevant exposures of ^{15}NO and O_2 alone on the clean surface. Coadsorption of ^{15}NO on preadsorbed O_2 resulted in significant changes to the TPD spectra of each molecule. Starting with O_2 (top in Figure 5), the amount of O_2 desorbing in 230 K TPD state was reduced by $\sim 75\%$ as a result of the influence of coadsorbed ^{15}NO . No O_2 was displaced from the surface during ^{15}NO dosing at 40 K so this change was due to surface chemistry. The 75% decrease in O_2 TPD peak area was considerably greater than the $\sim 20\%$ level seen from inherent O_2 dissociation on the clean surface (Figure 4). (The high temperature tail in the O_2 TPD data in Figure 5 is from O_2 desorption off the cryohead-cooled sample holder and not from the sample.) The presence of preadsorbed O_2 also had a significant impact on the surface chemistry of ^{15}NO . The most notable changes were in the significant decrease in the 370 K ^{15}NO peak and the appearance of a new ^{15}NO peak at 425 K. The total ^{15}NO TPD peak area was about the same with and without coadsorbed O_2 , with a slightly smaller amount in the coadsorbed case. In contrast, the 220 K ^{15}NO peak was not significantly affected by preadsorbed O_2 other than being broadened. The higher temperature edge of the 220 K peak coincided with a small $^{15}\text{NO}_2$ (mass 47) peak that desorbed at 240 K. (The mass 47 signal was also slightly above background in the temperature region near 425 K.) This suggests that the additional ^{15}NO desorbing on the high temperature side of the 225 K ^{15}NO peak was not part of that ^{15}NO state, but a new form of desorbing ^{15}NO (i.e., $^{15}\text{NO}_2$) that resulted from coadsorption with O_2 . The changes in the 230 K O_2 and 370 K ^{15}NO TPD states resulting from coadsorption suggests that the O_2 molecules in the former state react with ^{15}NO molecules in the latter state. As mentioned above, the pertinent sites are thought to be Fe^{2+} .

Figure 6 illustrates the consequences to the $^{15}\text{NO} + \text{O}_2$ reaction when the adsorption order was changed from O_2 first to ^{15}NO first. As in the previous figure, the gray traces shown in Figure 6 are for ^{15}NO and O_2 dosed alone on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface. TPD after adsorption of O_2 at 40 K on preadsorbed ^{15}NO is shown in the blue traces of Figure 6. The extent of reaction between these two molecules when O_2 was dosed on ^{15}NO was noticeably less than when ^{15}NO was dosed on O_2 , as gauged by the amount of ^{15}NO evolving at 425 K and the amounts of ^{15}NO and O_2 lost from the 370 and 230 K peaks, respectively. When preadsorbed ^{15}NO was preheated to 250 K first, which desorbed the 220 K ^{15}NO TPD state, subsequently dosed O_2 did not result in a significant reaction between ^{15}NO and O_2 , or much adsorbed O_2 at 230 K. This again suggests that ^{15}NO molecules in the 220 K TPD state were spectators to the NO oxidation reaction on this surface. (There was an appreciable amount of O_2 adsorbed in the 105 K state in the red trace, which coincided with the removed 220 K ^{15}NO state.) The ability of postdosed O_2 to react with ^{15}NO at 40 K (blue traces), but not when the ^{15}NO was preheated (red traces), suggests that at 40 K some adsorbed ^{15}NO molecules have not settled into 370 K binding sites, allowing subsequently adsorbed O_2 to reach those sites. In general, these data suggest that the oxidation reaction between ^{15}NO and O_2 requires O_2 to be chemisorbed at Fe^{2+} sites first.

Additional insights into the reaction of ^{15}NO and O_2 on $(\text{Fe,Cr})_3\text{O}_4(111)$ were obtained by employing $^{15}\text{N}^{18}\text{O}$. The $^{15}\text{N}^{18}\text{O}$ source utilized was 84% $^{15}\text{N}^{18}\text{O}$, 12% $^{15}\text{N}^{16}\text{O}$ and ~4% $^{14}\text{N}^{16/18}\text{O}$. (The ^{14}N -containing contributions were deemed small enough to be ignored.) Figure 7 presents TPD data for a set $^{15}\text{N}^{18}\text{O}$ exposure (13.6 Torr-s) on various preexposures of $^{16}\text{O}_2$. Only the NO TPD traces are presented in Figure 7 because no isotopic exchange was detected into the oxygen TPD. The gray traces are for $^{15}\text{N}^{16}\text{O}/^{15}\text{N}^{18}\text{O}$ on the clean surface. As the amount of $^{16}\text{O}_2$ preadsorbed was increased, the amount of the new products at 240 and 425 K also increased. Most notable though, the amount of $^{15}\text{N}^{16}\text{O}$ in these states was much greater than the amount of $^{15}\text{N}^{18}\text{O}$. This strongly indicates that the new ^{15}NO TPD states at 240 and 425 K were from decomposition of surface species in which $^{16}\text{O}-^{15}\text{N}^{18}\text{O}$ bonds were formed from a reaction of coadsorbed $^{16}\text{O}_2$ and $^{15}\text{N}^{18}\text{O}$. The isotopic scrambling of O into the new ^{15}NO TPD states at 240 and 425 K were not due to contributions from lattice oxygen since no scrambling was observed in the TPD experiment when $^{15}\text{N}^{18}\text{O}$ was dosed on the clean surface (gray traces). The ratio of $^{15}\text{N}^{16}\text{O}$ to $^{15}\text{N}^{18}\text{O}$ at 425 K indicates a reaction in which both ^{16}O atoms in the adsorbed O_2

become scrambled with the O atom brought to the surface by ^{15}NO . This suggests formation of a nitrate-like (NO_3) species and a general reaction stoichiometry according to Reactions 1 and 2:

The reaction stoichiometries in Reactions 1 and 2 also apply to the scrambling into the 240 K feature, but the species associated with this state is clearly different than that associated with the 425 K state. The data in Figure 7 also indicated that the 220 K ^{15}NO state is a spectator in the chemistry occurring between coadsorbed ^{15}NO and O_2 on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface as no scrambling was detected for this peak.

The discussion above process that ^{15}NO and O_2 react to form the new states responsible for the 240 and 425 K ^{15}NO TPD states. However, the oxidation reaction could involve a two step process in which O_2 dissociated first and then ^{15}NO reacted with atomic O, according to Reactions 3 and 4:

As the data in Figure 4 indicates, O_2 thermal dissociation occurred on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface during TPD. Data in Figure 8 explores the potential of Reactions 3 and 4 in the chemistry of ^{15}NO on $(\text{Fe,Cr})_3\text{O}_4(111)$. Two different surfaces with adsorbed atomic oxygen species were tested: the surface after a single O_2 TPD experiment and the surface after a single $^{15}\text{NO}+\text{O}_2$ TPD experiment (in both cases, limiting the TPD experiments to a maximum temperature of ~ 520 K). Subsequently dosed ^{15}NO on these surfaces showed no evidence of the new ^{15}NO states at either 240 or 425 K indicating that ^{15}NO does not react with atomic O on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface. Evidence that atomic O was present on the surface prior to adsorption of ^{15}NO was seen by significant decreases in amounts of ^{15}NO in the 370 K peak, with the displaced ^{15}NO appearing at 160 K. The ^{15}NO displaced (and hence the amount of O deposited) was greater for the O atom preparation method involving the $^{15}\text{NO}+\text{O}_2$ reaction than for the single O_2 TPD experiment. The deposition of atomic O (from either decomposition of O_2 or nitrate) had no influence on the 220 K ^{15}NO state, once again showing that the associated site (Fe^{3+}) was not involved in $^{15}\text{NO}+\text{O}_2$ chemistry.

3.4 Photochemistry of adsorbed ^{15}NO and O_2

Nitric oxide has been used as a probe molecule for the photochemical properties of various semiconducting oxide surfaces.^{28,30,32,34,53-57} Photodesorption is the dominant pathway for NO photochemistry on single crystal oxide surfaces under UHV conditions,^{24,26-28,32,34,35} and is a useful means of characterizing the photochemical properties of oxide surfaces. Figure 9 explores the photochemistry of $^{15}\text{N}^{18}\text{O}$ on the clean $(\text{Fe,Cr})_3\text{O}_4(111)$ surface using 460 nm light. After a 2 minute irradiation with 460 nm at 40 K, the majority of adsorbed $^{15}\text{N}^{18}\text{O}$ was depleted from the surface without appearance of any new TPD features reflective of new $^{15}\text{N}^{18}\text{O}$ states, photodecomposition or photo-induced scrambling with lattice oxygen. For example, there was no enhancement in the amount of $^{15}\text{N}^{16}\text{O}$ left on the surface or photodesorbed from the surface (data not shown) indicating that 460 nm light did not promote oxygen exchange with the lattice. Re-adsorption of $^{15}\text{N}^{18}\text{O}$ on the irradiated surface showed the identical TPD (not shown) to that on the clean surface (gray traces in Figure 9), indicating that no photodecomposition products (such as atomic O) were left on the surface. The ^{15}NO molecules that remained on the surface after 460 nm irradiation desorbed in a small peak at ~325 K. The ^{15}NO in this peak was resistant to photolysis compared to the photoreactivities of ^{15}NO in the 220 and 370 K peaks. As discussed in relation to Figure 1, the remaining ^{15}NO was reflects a less photoactive form of ^{15}NO on the surface, which was tentatively assigned to molecules bound at Cr^{3+} sites.³⁴

Figure 10 examines the effect of 460 nm irradiation on the coadsorption of $^{15}\text{N}^{18}\text{O}$ and $^{16}\text{O}_2$ on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface. The gray traces in Figure 10 are for the coadsorbed surface in the absence of 460 nm irradiation. Irradiation of $^{15}\text{N}^{18}\text{O}$ dosed on preadsorbed O_2 for 2 minutes at 40 K is shown with the blue traces. As was the case for irradiation of $^{15}\text{N}^{18}\text{O}$ on the clean surface, the majority of adsorbed $^{15}\text{N}^{18}\text{O}$ coadsorbed with O_2 was depleted from the surface by photodesorption (both for ^{15}NO and O_2). The amount of nitrate generated in the 425 K state was diminished by ~32% and the feature at 240 K was completely absent. This suggests that at 40 K (without preheating), 460 nm irradiation depletes the supply of ^{15}NO and O_2 from the surface, limiting the extent of nitrate formation during the subsequent TPD experiment. There was also the possibility that 460 nm irradiation might photodecompose any surface nitrates formed during the coadsorption process. Preheating the $^{15}\text{N}^{18}\text{O} + ^{16}\text{O}_2$ surface to 250 K prior to 460 nm irradiation (red traces) resulted in a slight increase in the amount of nitrate formed at 425 K (by ~9%) relative to the unirradiated surface. The ratio of $^{15}\text{N}^{16}\text{O}$ to $^{15}\text{N}^{18}\text{O}$ in the 425 K state

was not significantly affected by irradiation. The preheat to 250 K was sufficient to desorb all unreacted O₂, all unreacted ¹⁵N¹⁸O at 220 K and the nitrate species responsible for the 240 K state (see Figure 7). Irradiation with 460 nm light did not appear to photodecompose nitrate species in the 425 K state, but it also does not assist in promoting conversion of ¹⁵NO to nitrate. These results suggest that photodesorption is the main process for NO on the (Fe,Cr)₃O₄(111) surface and that any photochemical initiation of NO oxidation is a minor pathway compared to photodesorption.

4. Conclusions

The mixed Fe+Cr oxide termination formed on a mixed α -(Fe,Cr)₂O₃(0001) surface after sputter/anneal processing in UHV possessed a magnetite-like (111) surface structure. The active cation sites for NO adsorption were mostly Fe²⁺ and Fe³⁺, with minority amounts of Cr³⁺. The adsorption/desorption properties of NO and O₂ on this surface were similar, with binding at Fe²⁺ and Fe³⁺ sites resulting in well-resolved TPD states. The binding of NO and O₂ at the Fe²⁺ sites was more stable than at Fe³⁺ sites. A significant difference between NO and O₂ was that ~10% O₂ thermal dissociation occurred in TPD whereas no NO decomposition was observed. Coadsorption of NO and O₂ results in at least two different types of surface nitrates. The reactions occurred only at Fe²⁺ sites and predominately if O₂ was adsorbed first. The resulting nitrates thermally decomposed to NO during TPD, leaving atomic oxygen on the surface. Atomic O was not active for NO oxidation. Irradiation of NO or NO+O₂ on the surface with 460 nm light did not promote photooxidation. Nitrates formed from a thermal reaction of NO+O₂ were insensitive to irradiation. Results in this study provide support for Fe²⁺ being the active sites for NO oxidation in Fe-containing SCR catalysts.

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Figure 1

^{15}NO (mass 31) TPD spectra from various ^{15}NO exposures on the clean $(\text{Fe,Cr})_3\text{O}_4(111)$ surface at 40 K. The inset shows the total ^{15}NO TPD peak area as a function of exposure.

Figure 2

King & Wells sticking coefficient measurements for ^{15}NO (mass 31) on the clean $(\text{Fe,Cr})_3\text{O}_4(111)$ surface at 40 (blue trace) and 450 K (black trace). (The latter indicates the level of full beam reflection from the crystal.) The ^{15}NO pressure was built up in the molecular beam doser prior to time '0', at which time the shutter was opened exposing the surface to the ^{15}NO beam. (A non-effusive contribution of gas leaving the doser was estimated at $\sim 3\%$ from the signal level prior to opening the shutter.)

Figure 3

O₂ (mass 32) TPD spectra from various O₂ exposures on the clean (Fe,Cr)₃O₄(111) surface at 40 K. The inset shows the total O₂ TPD peak area as a function of exposure.

Figure 4

O₂ (mass 32) TPD spectra for consecutive O₂ exposures (~23 Torr-s) on the (Fe,Cr)₃O₄(111) surface at 40 K. In each experiment, the surface was dosed with O₂ at 40 K after the previous O₂ TPD experiment was concluded at ~520 K without heating the surface to 900 K, except for spectra #1 and 7. The inset shows the 230 K O₂ TPD peak area for each cycle.

Figure 5

TPD spectra for O_2 (mass 32), ^{15}NO (mass 31) and $^{15}\text{NO}_2$ (mass 47) from a 13.6 Torr-s ^{15}NO exposure on a 28 Torr-s O_2 exposure, both at 40 K, on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface. The surface was heated to 120 K after O_2 adsorption and prior to ^{15}NO . O_2 and ^{15}NO spectra are displaced vertically for clarity. Gray traces are for the same ^{15}NO and O_2 exposures alone, with the latter preheated to 120 K prior to TPD.

Figure 6

TPD spectra for O_2 (mass 32) and ^{15}NO (mass 31) from a 28 Torr-s O_2 exposure on a 13.6 Torr-s ^{15}NO exposure, both at 40 K, on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface. The surface was not heated between ^{15}NO and O_2 (blue traces) or heated to 250 K between ^{15}NO and O_2 (red traces). O_2 spectra are displaced vertically for clarity. Gray traces are for the same ^{15}NO and O_2 exposures alone.

Figure 7

TPD spectra for $^{15}\text{N}^{18}\text{O}$ (mass 33) and $^{15}\text{N}^{16}\text{O}$ (mass 31) from a 13.6 Torr-s $^{15}\text{N}^{18}\text{O}$ exposure on various O_2 exposures, both at 40 K, on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface. (The $^{15}\text{N}^{18}\text{O}$ source possessed $\sim 12\%$ $^{15}\text{N}^{16}\text{O}$ and $\sim 4\%$ ^{14}NO isotopes as impurities.) $^{15}\text{N}^{18}\text{O}$ spectra are displaced vertically for clarity.

Figure 8

^{15}NO (mass 31) TPD spectra from a 13.6 Torr-s exposure on the clean $(\text{Fe,Cr})_3\text{O}_4(111)$ surface at 40 K (gray trace), and for the same ^{15}NO exposure on the surface after an O_2 TPD experiment to 520 K (red trace) and after a coadsorbed $^{15}\text{NO}+\text{O}_2$ TPD experiment to 520 K (blue trace).

Figure 9

TPD spectra for $^{15}\text{N}^{18}\text{O}$ (mass 33) and $^{15}\text{N}^{16}\text{O}$ (mass 31) from a 13.6 Torr-s $^{15}\text{N}^{18}\text{O}$ exposure on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface at 40 K both with (blue traces) and without (gray traces) 460 nm irradiation at 40 K. (The $^{15}\text{N}^{18}\text{O}$ source possessed $\sim 12\%$ $^{15}\text{N}^{16}\text{O}$ and $\sim 4\%$ ^{14}NO isotopes as impurities.) $^{15}\text{N}^{18}\text{O}$ spectra are displaced vertically for clarity.

Figure 10

TPD spectra for $^{15}\text{N}^{18}\text{O}$ (mass 33) and $^{15}\text{N}^{16}\text{O}$ (mass 31) from a 13.6 Torr-s $^{15}\text{N}^{18}\text{O}$ exposure on a 28 Torr-s O_2 exposure, both at 40 K, on the $(\text{Fe,Cr})_3\text{O}_4(111)$ surface, both with (blue traces) and without (gray traces) 460 nm irradiation at 40 K. The red traces are from preheating the surface to 250 K prior to 460 nm irradiation. (The $^{15}\text{N}^{18}\text{O}$ source possessed $\sim 12\%$ $^{15}\text{N}^{16}\text{O}$ and $\sim 4\%$ ^{14}NO isotopes as impurities.) $^{15}\text{N}^{18}\text{O}$ spectra are displaced vertically for clarity.

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