**Oxidation of Zeolite Acid Sites in NO/O₂ Mixtures and the Catalytic Properties of the New
Site in NO Oxidation**

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Abstract

The NO oxidation reaction kinetics over a number of zeolite structures were investigated at temperatures above 423 K using plug-flow microreactors and *in situ* FTIR spectroscopy. Fast catalytic NO oxidation rates (up to 1,000 $\times$) are observed over H- and Na-exchanged zeolite frameworks (BEA, MFI, and CHA) at temperatures above 423 K with respect to the gas-phase reaction. NO oxidation rates increase with temperature over H- and Na-zeolites, while siliceous zeolites display little activity. Activation energies scale in the order of CHA < MFI < BEA (40.8-55.5 kJ mol⁻¹), and application of transition state theory shows that the formation of the activated complex is an enthalpically controlled process that benefits from smaller zeolite pore size. In all samples, rates are proportional to NO and O₂ concentrations, in contrast to low temperature catalytic rates (*J. Catal.*, **2014**, 311), which are second order in NO and first order in O₂. This difference indicates that a new reaction mechanism is operative above 423 K. *In-situ* FTIR studies reveal that NO⁺ coordinated at framework sites in the zeolite pores (Si–O[–](NO⁺)–Al) play a direct role in the catalysis, and they also reveal that the NO oxidation rate is proportional to the amount of NO⁺ present in the sample. Furthermore, it is found that NO⁺ is in equilibrium with gas phase NO and that desorption of NO⁺ (as NO) yields an oxidized acid site (Si–O[–]–Al). No evidence of NO⁺ formation is observed over the siliceous zeolite samples. A working model of the reaction mechanism for the high-temperature NO oxidation reaction is proposed for acidic zeolites that is consistent with the observed form of the rate equation and the observed NO⁺ reaction intermediate.

Keywords: NO oxidation, SSZ-13, chabazite, environmental catalysis, NH₃ SCR, NO₂

1. Introduction

The homogeneous gas phase nitric oxide (NO) oxidation by O₂ is peculiar in the sense that the reaction rate constant decreases with increasing temperature, resulting in irregular Arrhenius behavior and yielding a negative apparent activation energy ($\sim -4.4 \text{ kJ mol}^{-1}$) [1]. The reaction is second order in NO and first order in O₂, a dependency that has been verified at total pressures between 25 mbar and 1 bar. The *catalytic* NO oxidation is an important reaction in a number of chemical processes, with applications ranging from environmental chemistry (NO_x reduction) to the production of valuable chemical products such as nitric acid and aromatic nitrates [2]. The reaction is currently investigated in the context of diesel emissions control technologies to abate the release of nitrogen oxides (NO_x). One such technology is the selective catalytic reduction with ammonia (NH₃-SCR) of NO_x using zeolite catalysts, an effective and widely utilized post-combustion treatment method that converts these pollutants into nitrogen and water [3]. Fe- or Cu-exchanged zeolites, particularly high-silica chabazites (CHA), such as SSZ-13, are efficient catalysts for SCR technology, capable of maintaining high levels of NO_x conversion over a wide temperature range [4-7].

The importance of NO oxidation in SCR over zeolites is unclear and seems dependent on the catalyst, as sometimes it has been implicated as the overall rate-determining step (RDS) [8-14], while in other cases it has been shown to not be the RDS [15, 16]. Nonetheless, Verma et al. [17] have recently shown that NO oxidation can be a useful probe reaction for better understanding of the SCR process. NO oxidation also plays a significant role in NO_x-mediated homogenous pathways of CH₄ oxidation to produce formaldehyde (HCHO). Iglesia and coworkers [18] have shown that CH₄-O₂ mixtures in the presence of NO_x, particularly NO₂, exhibit significant reaction rates increases and HCHO yield. Lastly, NO oxidation is part of nitric

acid synthesis via the Ostwald process (eq. 1-3). An effective catalyst for NO oxidation (eq. 2) at high temperatures would enable the gas to be directly converted without the need for a cooling stage in the process.

There have been many investigations of the kinetics and reaction mechanism of NO oxidation over metal-containing zeolites, particularly with copper and iron species [19-21]. Less attention has been given to the high-temperature NO oxidation mechanism over materials without transition metals. Early reports by Halasz et al. [22, 23] showed that H-ZSM-5 was capable of catalyzing the NO oxidation, while Li-ZSM-5 showed minimal activity at temperatures above 473 K. The authors suggested that the Brønsted acid sites were the likely active sites for the reaction above 473 K. Järås and co-workers [13, 24, 25] studied NO oxidation over mordenite (MOR) zeolites, and ranked zeolite catalysts based on observed reaction rates in the order of H-MOR > Fe-MOR > Cu-MOR for NO oxidation, but in the reverse order for the NO reduction using the NH₃-SCR. The NO oxidation rate was dependent on the aluminum content for the H-MOR catalyst, and the authors suggested that surface NO⁺ is involved in the catalytic cycle [25]. Yogo and coworkers [26-28] observed that the NO oxidation rate over Na/H-ZSM-5 increased with increasing proton exchange level, deducing that acid sites in ZSM-5 were responsible for the activity. They also noted a strong inhibition of the reaction by water. Stakheev et al. [29] found that H-ZSM-5 was in fact more active than Co/H-ZSM-5 catalysts with low levels of Co exchange (< ~30%), and suggested that the Co ions only become

catalytically active at increased loadings when cobalt oxide particles form. Lonyi et al. [30] recently observed activity over H-ZSM-5 at temperatures between 573 and 823 K, though it was substantially lower compared to Co-H-ZSM-5; the activity of H-ZSM-5 was assigned to the Brønsted acid sites, though they did not propose a reaction mechanism. Miller et al. [31] observed acid forms of ZSM-5 and MOR to be effective for NO oxidation at 573 K, while USY and silica-alumina exhibited poor activity. Other recent reports [32, 33] have shown that siliceous zeolites and microporous materials can catalyze very effectively NO oxidation at temperatures below 423 K.

In-situ infrared (IR) spectroscopy techniques are often applied to characterize the structure and stability of N_xO_y surface species. Previous reports [30, 34-39] have examined NO/O₂/NO₂ adsorption on zeolites to identify N_xO_y adsorbates that may have a role in the NO oxidation reaction: many surface species are present, especially at low temperatures. The nitrosonium ion (NO^+) is frequently observed because of its mechanistic importance in NH₃-SCR and NO oxidation. There is general agreement that NO^+ exhibits an IR signature around 2100-2200 cm⁻¹, although uncertainty remains about the conditions under which it is stable and its precise role in the mechanisms of NH₃-SCR and NO oxidation over various catalysts. The importance of NO^+ in NH₃-SCR may be linked to ammonium nitrite (NH₄NO₂), a key reaction intermediate that decomposes quickly into nitrogen and water. The nitrogen atoms from the ammonium group and nitrite group in NH₄NO₂ have formal oxidation states of 3- and 3+, respectively. NO^+ and NO_2^- (nitrite) are the only N_xO_y species with nitrogen in a 3+ formal oxidation state.

Recently, we reported that NO oxidation at temperatures below 423 K is catalyzed by several kinds of microporous materials, such as activated carbons, metal-organic frameworks

(MOFs), and zeolites in the proton, sodium, and siliceous form [33]. Measured rates were observed to be ~ 100 - $10,000$ times larger than the homogeneous phase reaction rates. The catalytic properties of the materials were attributed to their ability to stabilize a $[\text{N}_2\text{O}_4]^\ddagger$ transition state within the micropores through non-covalent van der Waals and electrostatic forces. This confinement effect accelerates the homogenous-like reaction and leads to large and negative activation energies ($-24.9 \text{ kJ mol}^{-1}$ to $-37.5 \text{ kJ mol}^{-1}$) compared to the homogeneous phase reaction (-4.4 kJ mol^{-1}).

In this report we examine the NO oxidation reaction at high temperatures ($T > 423 \text{ K}$) catalyzed by three zeolite frameworks (CHA, MFI, BEA) and have investigated the effect of Si/Al ratio and the extra-framework cation (H^+ , Na^+ and siliceous) on NO oxidation rates. The results show that NO oxidation is catalyzed effectively over H- and Na-exchanged zeolites (BEA, MFI, and CHA), and that the zeolite structure and composition considerably affect NO oxidation rates. We have used *in-situ* Fourier transform infrared (FTIR) spectroscopy to monitor N_xO_y surface species formed on zeolite materials, and show that NO^+ coordinated to framework aluminum sites within the zeolite pores are directly involved in the catalysis. FTIR studies also reveal that NO^+ is in equilibrium with gas phase NO, and that desorption of NO^+ (as NO) results in an oxidized zeolite site. Based on these data we propose a reaction mechanism for the catalytic high temperature NO oxidation over high silica H-SSZ-13 (CHA).

2. Materials and Methods

2.1 Material synthesis and characterization

Pure-silica and alumino-silicate samples of SSZ-13 (CHA) were prepared using a previously reported synthesis procedure [33]. ZSM-5 (MFI) materials with Si/Al ratios of 12 and

18 were synthesized using a procedure described by Kim et al. [40]. Commercial forms of zeolite beta (BEA) (CP 814E*, Si/Al = 12.5; CP 814C*, Si/Al = 19) and ZSM-5 (CBV 8014, Si/Al = 40; CBV 28014, Si/Al = 140) were obtained from Zeolyst International. Samples were calcined in air at 823 K for 8 h using a ramping rate of 180 K h⁻¹ to generate the Brønsted acid sites from the ammonium-form of zeolite.

Powder X-ray diffraction (XRD) patterns were collected using a Phillips X'pert diffractometer with a Cu K α source. Textural characterization of the samples was determined using N₂ physisorption at 77 K. Isotherms were collected on a Micrometrics ASAP 2020 and analyzed using the t-plot method to calculate microporous volumes. Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX) spectra were collected on a JEOL JSM7400F microscope to provide information regarding sample morphology and elemental composition, respectively. ²⁹Si and ²⁷Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of zeolite samples were recorded on a Bruker AVIII-500 solid-state NMR spectrometer. The spectrometer was operated at a Larmor frequency of 500.138 MHz for ¹H and 99.362 MHz for ²⁹Si. A 4-mm HX MAS probe was used for all measurements. All spectra were recorded at a MAS frequency of 10 kHz, controlled to within ± 2 Hz using a Bruker MAS controller. ²⁹Si single pulse and cross-polarization (CP) measurements have been performed as well. For ²⁹Si single pulse MAS experiments, a 90° pulse with a width of 4.3 μ s was used and the recycle delay was 30 s. For {¹H}-²⁹Si CP MAS experiments, the ¹H 90° pulse duration was 2.5 μ s. A linear amplitude ramp (80-100%) on ¹H was used with a contact time of 4.5 ms, and the recycle delay was 5 s. SPINAL64 ¹H decoupling with an RF field strength of 100 kHz was applied during the acquisition period for both SP and CP MAS measurements. For ²⁷Al single-pulse MAS experiments, a 90° pulse with a width of 1.25 μ s was used with a recycle delay of 1 s.

Silicon resonance intensities in the NMR spectra were used to estimate Si/Al ratios of the zeolite materials according to eq. 4, where I is the intensity of a particular silicon resonance and n is the number of coordinated Al atoms for that resonance. Deconvolution techniques were used to accurately determine the intensities of overlapping resonances. Elemental analysis was also carried out using inductively coupled plasma (ICP) mass spectrometry.

$$Si/Al = \frac{\sum_{n=0}^4 I_{Si(n\ Al)}}{\sum_{n=0}^4 0.25\ n\ I_{Si(n\ Al)}} \quad (4)$$

2.2 NO oxidation rate measurements

NO oxidation rates were measured using a differential reactor flow system. Powder zeolite samples (100 mg) were placed on a porous quartz frit within a U-shaped quartz reactor (10 mm O.D.). Reactant gases (2% NO/He, 1% NO₂/He, 15% O₂/He) and He carrier gas (99.995%) were controlled using electronic mass flow controllers (Brooks 5850E series) to provide a range of inlet reactant partial pressures (0.02-0.10 kPa NO, 1-5 kPa O₂, 0.005-0.05 kPa NO₂) at a total flow rate of 100 sccm. Zeolite catalysts were treated in flowing 10% O₂/He at 793 K for 2 h prior to catalytic rate measurements. The lines into and out of the reactor were heated at 393 K to avoid any condensation and minimize surface adsorption effects. Reactions were conducted isothermally over the temperature range of 423-623 K by placing the reactor within a temperature programmable furnace (ATS Series 3210 split tube furnace with Watlow EZ-Zone PM temperature control). The catalyst temperature was monitored by the insertion of a thermocouple (Omega, K-type, 1/16 in. diameter) through the top of the reactor and placing it near the catalyst sample. Outlet stream concentrations were monitored using a heated transmission infrared (IR) gas cell (Specac Cyclone C2 fixed 1 M pathlength) within a Fourier transform infrared (FTIR) spectrometer (Nicolet Nexus 470). The spectrometer was equipped

with an MCT-A (mercury cadmium telluride) detector and operated at resolution of 4 cm^{-1} . 80 scans were collected at an optical velocity of 0.9494.

NO oxidation rate measurements are reported on a specific basis ($\text{mol s}^{-1} \text{g}_{\text{cat.}}^{-1}$) and as turnover frequencies (s^{-1}) per acid site for H-form zeolites. NO conversions were maintained below 10% for all measurements to ascertain differential reaction conditions. Control experiments were conducted in the absence of a catalyst to assess the contribution of the gas-phase reaction and reactor to observed reaction rates. Reaction orders α , and β , and γ with respect to NO, O_2 , and NO_2 were measured over the different catalysts by analyzing the rate dependency on reactant concentration using the relation (eq. 5):

$$r_{\text{NO}_2} = \frac{k_{\text{app.}}[\text{NO}]^\alpha[\text{O}_2]^\beta}{1+K[\text{NO}_2]^\gamma} \quad (5)$$

Eq. 6 and 7 were used to model the reaction and obtain the rate constants and associated kinetic parameters in the cases of the absence or presence of NO_2 in the feed gas, respectively.

$$r_{\text{NO}_2} = k_{\text{app.1}}[\text{NO}]^\alpha[\text{O}_2]^\beta \quad (6)$$

$$r_{\text{NO}_2} = k_{\text{app.2}}[\text{NO}]^\alpha[\text{O}_2]^\beta[\text{NO}_2]^{-\gamma} \quad (7)$$

2.3 In-situ IR studies

A flow system was used to introduce NO/ O_2 / NO_2 gas mixtures onto the zeolite samples during FTIR spectroscopy surface experiments. He, NO, NO_2 and O_2 from calibrated mixtures with He were sent to the reaction chamber at a total flow rate of 100 sccm by mass flow controllers (Brooks 5850E series). Typical inlet concentrations consisted of combinations of 500-2,000 ppm NO, 5% O_2 , and 100 ppm NO_2 to approach gas compositions of combustion gases.

Moisture removal purifiers containing molecular sieve 5A (Chromatography Research Supplies, Model 500) were placed directly after the He and O₂ gas cylinders. Tests were carried out using the same spectrometer described above. The spectrometer was operated at a spectral resolution of 4 cm⁻¹, and the obtained spectra were averaged from 100 collected scans. OMNIC software was used to collect IR spectral data. The IR spectra presented in this report represent those that reached steady-state under the conditions listed. Zeolite samples were loaded into an *in-situ* transmission infrared cell, which was built in accordance with the original design by the Ribeiro group [41]. Briefly, the FTIR cell is comprised of a cell body, sample holder, and aluminum heating block. Approximately 50 mg of zeolite was required to make the sample pellet/wafer, which was loaded onto the sample holder disks. The sample holder was held in place within the cell body along the IR beam path. CaF₂ IR-grade windows (25.4 mm diameter, 10 mm thickness, Redoptronics) were chosen to provide a spectral range of 4000-1100 cm⁻¹. Gas lines connected to the cell body allowed the gases to contact the samples in a controlled flow pattern. A heating block housed the assembled IR cell, and utilized 4 heating rods (McMaster Carr, 125 W) connected to a temperature controller (Omega CSI32K benchtop controller) to regulate the sample temperature. A thermocouple (Omega, K-type, 1/16 in. diameter) was positioned through an insert in the cell body to measure the sample temperature. Zeolite samples were pre-treated in 15% O₂/He at 573 K (300 K/h ramp rate) for 3 h to remove adsorbed water and other surface contaminants. Afterwards, background spectra of the activated samples were collected at the temperatures for which the studies were conducted.

3. Results and Discussion

3.1 Materials characterization

Powder XRD patterns confirmed that all zeolite samples were highly crystalline with the expected framework structures and revealed no impurities (see Figure S.10 in the Supporting Information). Microporous volumes and external surface areas were determined from the analysis of the N₂ adsorption isotherms (Table 1). These data are all consistent with samples of high crystallinity. EDX chemical analyses of the zeolite samples were used to estimate the Si/Al ratios. Solid-state magic-angle-spinning NMR (²⁹Si and ²⁷Al) confirmed that the content of extra-framework aluminum species was low for all zeolite samples (see Figure S.14 in the Supporting Information). Framework Si/Al ratios were also estimated from the solid-state MAS NMR spectra (Table 1).

3.2 *Effect of temperature, zeolite structure, and extra-framework cation on NO oxidation rates*

NO oxidation rates were measured as a function of temperature from 298-623 K over H-, Na-, and siliceous CHA materials to observe the effects that aluminum atoms and the extra-framework cation (H⁺, Na⁺) have on reactivity (Figure 1). NO₂ was the only product observed, with no detectable quantities of N₂O or any other side products. The materials exhibit two reaction regimes as a function of temperature, as indicated by the V-shape curve in Figure 1. Below a temperature of approximately 423 K, all materials display substantial catalytic reactivity, and reaction rates *decrease* with increasing temperature, resulting in negative apparent activation energies (-24.9 to -37.5 kJ mol⁻¹). These low-temperature results have been described previously [32, 33], with the catalytic activities attributed to a confinement effect in the materials' micropores that accelerate a homogeneous-like reaction by stabilizing a N₂O₄[‡] transition state inside the zeolite crystals.

The trend with temperature changes above 423 K, and reaction rates over H-SSZ-13 and Na-SSZ-13 increase with increasing temperature (left-hand side of V curve), a clear indication that a different reaction mechanism occurs above 423 K. The reaction rates over *siliceous* CHA are low and unaffected by temperature above 423 K, indicating that the material has minimal catalytic activity in this temperature regime. This is in contrast to the alumino-silicate samples, which showed significant catalytic rates, approximately 10-100 times than those over siliceous CHA. Note that thermodynamic equilibrium limitations become significant at temperatures greater than 623 K (beyond the maximum temperature investigated here), and our measurements did not indicate any substantial influence of the reverse reaction at the temperatures investigated.

Above 423 K reaction rates scale as follows: H-SSZ-13 > Na-SSZ-13 > pure-silica CHA. This differs from the order below 423 K, where reaction rates were highest for Na-SSZ-13, followed by H-SSZ-13 and pure-silica CHA. The higher activity for H-SSZ-13 compared to Na-SSZ-13 at high temperatures is consistent with an earlier report by Halasz et al. [23] that showed fast catalytic rates for H-ZSM-5 but substantially lower rates for Li-ZSM-5. In both instances, the proton form of the zeolite shows faster reaction rates than the alkali metal-exchanged zeolite. This difference in catalytic rates indicates that the acid site is directly involved in the catalytic reaction. The observation that pure-silica CHA is inactive above 423 K further supports the notion that framework aluminum atoms with exchanged cations are necessary to observe activity. In the high-temperature regime, reaction rates over H-SSZ-13 change more rapidly with temperature compared to those over Na-SSZ-13. We also found that reaction rates were independent of the starting temperature; that is, proceeding from high to low temperature and from low to high temperature resulted in the same reaction rates (see Figure S.4 in the Supporting Information). The apparent activation energy (E_a) obtained from the Arrhenius plots

in Figure 1 using the data above 423 K is 18.2 kJ mol^{-1} for Na-SSZ-13 and 39.6 kJ mol^{-1} for H-SSZ-13. The difference is substantial and suggests differences in the reaction mechanism for the Na^+ versus the acid sample in this high temperature regime (see below). This is the opposite of what is observed at low temperatures, where the sodium sample has higher (more negative) activation energy than the proton sample, a difference that was attributed to the larger electrostatic interaction between the sodium cation and the transition state, than is the case with the acid sample.

To assess the effect of the zeolite structure on the NO oxidation reaction, rates were measured as a function of temperature in the high temperature regime (423-623 K) over three zeolites (CHA, MFI, BEA) in the proton form and with Si/Al ratios ranging from 6-140. Note that the three frameworks have different pore systems: CHA is a small-pore zeolite with a three-dimensional 8-membered rings pore system ($3.72 \text{ \AA}$ diameter), MFI is a medium-pore zeolite with 10-membered rings ($\sim 5.6 \text{ \AA}$ diameter), and BEA is a large-pore zeolite with 12-membered rings ($\sim 7.6 \text{ \AA}$ diameter). Reaction rates are plotted as turnover frequencies (TOFs) per mol of Brønsted acid sites in Figure 2. The order of NO oxidation rate is: H-SSZ-13 > H-ZSM-5 > H-BEA. This trend suggests that reaction rates increase with decreasing pore size. Turnover frequencies for each framework were found to be relatively consistent and independent of Si/Al ratio; however, TOF variation was observed to be as high as $\sim 20\%$ at certain temperatures over the H-ZSM-5 framework. Additionally, TOFs over H-ZSM-5 with Si/Al = 12 were consistently greater than those over H-ZSM-5 with Si/Al = 18 as a function of temperature; this may be due to site-site interactions in H-ZSM-5 that are more prevalent in this zeolite because it has a lower microporous volume than beta or chabazite (at a given Si/Al ratio). The reaction rates over the three zeolite frameworks are affected differently by temperature, with H-BEA having a $E_a = 54.2$

kJ mol^{-1} , and H-ZSM-5 and H-SSZ-13 having activation energies of 45.1 kJ mol^{-1} and 35.9 kJ mol^{-1} , respectively. Consequently, a larger difference between reaction rates is observed at lower temperatures of the reaction regime, while at higher temperatures, the differences in reactivity become smaller. The observed TOFs can be compared to reported values for NH_3 -SCR to determine whether or not the NO oxidation reaction is kinetically relevant to the SCR reaction. Ellmers et al. [42] reported a TOF of $\sim 2.5 \times 10^{-3} \text{ s}^{-1}$ over Fe-ZSM-5 at 523 K under a feed of 1,000 ppm NO, 1,000 ppm NH_3 , and 2% O_2 , which is several orders of magnitude greater than the TOFs we measured ($8 \times 10^{-5} \text{ s}^{-1}$ over H-SSZ-13 and $5 \times 10^{-5} \text{ s}^{-1}$ over H-ZSM-5) for NO oxidation at the same temperature. Thus, it appears that although the zeolites used in this study are quite active in catalyzing the NO oxidation reaction relative to the gas-phase reaction, the observed rates are still significantly lower than those for standard SCR.

3.3 Reaction orders with respect to NO, O_2 , and NO_2

NO oxidation rates were measured over H-SSZ-13 (Si/Al = 12) varying the NO, O_2 , and NO_2 inlet concentrations to determine reaction orders (α , β , and γ) for NO, O_2 , and NO_2 , respectively, at 473 K (Figure 3). The following rate expression (eq. 8) accurately fits the reaction rate data:

$$r_{\text{NO}_2} = k_{app} [\text{NO}] [\text{O}_2] [\text{NO}_2]^{-1} \quad (8)$$

NO oxidation rates are proportional to NO and O_2 concentrations, and inversely proportional to NO_2 over the range of investigated inlet concentrations. These reaction orders have been observed previously by Weiss and Iglesia [43, 434] over $\text{Pd}/\text{Al}_2\text{O}_3$ and $\text{Pt}/\text{Al}_2\text{O}_3$ under similar reaction conditions. Note that these reaction orders differ from those found in the low temperature reaction regime (2 for NO and 1 for O_2), providing further evidence that a change in

the reaction mechanism occurs at ~423 K [32, 33]. Residual error plots of the data fit in Figure 3 were examined to verify that the variation of the residuals was random (see Figures S.11-S.13 in the Supporting Information). The plots show no discernible patterns or trends, indicating that the reaction rate model describes the observed behavior adequately. Reaction orders for the acid form of the other zeolites structures (ZSM-5, BEA) at high temperature were found to be similar (see Table S.1 in the Supporting Information). The agreement of the reaction orders for all of the materials at high temperatures suggests a similar NO oxidation reaction mechanism: differences in activation energy are most likely due to the difference in stabilization of the transition state by the various zeolites.

Table 2 summarizes reaction rates, turnover frequencies (TOF), and kinetic parameters (E_a , k_o) for the high temperature NO oxidation over H-SSZ-13, H-ZSM-5, and H-BEA with Si/Al ratios near 12. The rate constants were calculated assuming the experimentally observed reaction orders (first order with respect to NO and O₂). The reaction rate over H-SSZ-13 at 473 K is approximately two times larger than the rate over H-ZSM-5 and about 8 times larger than the rate over H-BEA. Apparent activation energies estimated over the temperature range of 423-623 K for H-SSZ-13 (Si/Al = 12), H-ZSM-5 (Si/Al = 12), and H-BEA (Si/Al = 12.5) are 39.6 kJ mol⁻¹, 45.1 kJ mol⁻¹, and 54.2 kJ mol⁻¹, respectively. Note that as pore size increases, activation energy increases. The lower activation energy for H-SSZ-13 indicates that there is a greater enthalpic stabilization to the transition state compared to the other zeolite frameworks ($E_a = \Delta H^\ddagger + mRT$). Previous kinetic studies of high-temperature NO oxidation over zeolites and other catalytic materials have reported a wide range of apparent activation energies (Table 3) [13, 15, 17, 45-51]. The activation energies measured in this study fall within the broad range of these reported values (8.9-75.3 kJ mol⁻¹).

Average TOFs and kinetic parameters (E_a , k_o) were calculated for each zeolite framework with different Si/Al ratios (Table 4) based on the data from Figure 2. Activation energies for each framework type with different Si/Al ratios were found to be in good agreement and thus independent of the Si/Al ratios tested. Greater variation was seen for H-ZSM-5 compared to the other zeolite frameworks; the origin of this variability remains uncertain.

3.4 In-situ IR spectroscopy studies of N_xO_y surface species over SSZ-13 zeolites at temperatures between 423-623 K

In-situ IR spectroscopy experiments were conducted to examine N_xO_y surface species formed on the zeolite under reaction conditions from exposure to flowing gas mixtures of NO, O₂, and NO₂. The aim is to identify relationships between the species observed by IR spectroscopy and catalytic activity. H-SSZ-13 was chosen for this investigation since it showed the highest NO oxidation activity in the high-temperature reaction regime (423-623 K) and has a simpler structure than MFI or beta. We monitored in particular the presence of the nitrosonium ion (NO⁺), which has been observed to form during NO oxidation over zeolites at low temperatures [34-39]; these reports, however, have not investigated the N_xO_y surface species that form at elevated temperatures. Additionally, it is known that NO⁺ plays a role in the NH₃-SCR reaction mechanism over certain metal-exchanged zeolites [52-55]. NO⁺ formation over acid zeolites occurs at low temperatures through the heterolytic dissociation of N₂O₄ at Brønsted acid sites (eq. 9).

Because of the charge of NO⁺, it can ion-exchange with the proton in the Brønsted acid site. N₂O₄ is present from the dimerization of NO₂, a reaction that is favored inside the zeolite pore at

low temperatures. At the high temperatures investigated here, however, it is uncertain if this mechanism is responsible for NO^+ formation. Above 390 K, the equilibrium between NO_2 and N_2O_4 results in very low N_2O_4 concentrations, suggesting that an alternate mechanism may be responsible for NO^+ formation at temperatures above this point.

Figure 4 shows the IR spectra over H-SSZ-13 resulting from the adsorption of NO and co-adsorption of NO and O_2 at 573 K. Initially, gas containing 1,000 ppm NO is fed to the IR cell/reactor and no detectable changes in the spectra are observed (red line in Figure 4). After introducing O_2 (5% v/v)—in addition to the 1000 ppm of NO—to the gas flowing into the IR cell, two intense IR bands are observed: a positive band at 2185 cm^{-1} , and a negative band at 3610 cm^{-1} (blue line in Figure 4). We did not detect any absorbances associated with adsorbed N_2O_4 (typically observed at 1745 cm^{-1}) at these elevated temperatures. The IR absorption peak at 2185 cm^{-1} is characteristic of NO^+ in zeolites, which has been identified between $2133\text{--}2200\text{ cm}^{-1}$ depending on the zeolite structure and the concentration of the NO/ O_2 gas mixture [56-58]. This result demonstrates the ability of NO^+ to form at high temperatures, in agreement with the result obtained by Lonyi et al. [30] over H-MOR. The negative absorbance at 3610 cm^{-1} results from the disappearance of Brønsted acid sites due to the replacement of the proton with NO^+ . Other commonly found adsorbed N_xO_y species at low temperatures (NO_3^- , NO_2^- , N_2O_4 , NO_2 , N_2O_3) were not observed, possibly because they do not remain on the surface at such high temperatures [34-39]. NO^+ is the only stable surface species observed at elevated temperatures, and thus is potentially a reaction intermediate in the observed NO oxidation activity.

After turning off the O_2 flow it is observed that under 1,000 ppm NO, the NO^+ IR signal remains stable but at a reduced intensity as compared to the case when O_2 was present (yellow line in Figure 4). Concurrently, the acid site signal at 3610 cm^{-1} becomes less negative, but does

not diminish completely. The OH signal that remains could be due to water impurities within the cell, as the reaction between NO^+ and water yields acid sites (eq. 10). Additional evidence for the presence of water is indicated by the broad signal around 3400 cm^{-1} , which is characteristic of -OH vibrational modes for hydrogen bonded species at Brønsted or silanol sites, and the sharp peak at 3575 cm^{-1} , which represents the $\nu_s(\text{H}_2\text{O})$ vibrational mode for molecularly adsorbed water [58].

In the absence of NO or O_2 , the NO^+ signal decreases monotonically until it disappears entirely after several minutes under He flow (green line in Figure 4). Gas containing 1,000 ppm NO was then reintroduced and an immediate restoration of the NO^+ IR signal at 2185 cm^{-1} (purple line in Figure 4) is observed. The reappearance of the NO^+ *in the absence* of O_2 suggests that the zeolite acid site has been altered to allow for an alternative route of NO^+ formation. Under initial conditions, NO^+ did not form from exposure to 1,000 ppm NO; however, once the NO^+ was generated by co-adsorption of NO and O_2 , then NO^+ could reform in the presence of only NO. This result suggests an electron-transfer reaction involving lattice oxygen atoms of the zeolite framework and NO^+ (eq. 11).

In the presence of NO or NO/ O_2 gas mixtures, the NO^+ species at Brønsted acid sites is stable ($Z\text{NO}^+$). However, under an inert gas (flowing He), NO^+ leaves the surface and in the process accepts an electron from the zeolite to become NO in the gas phase, leaving behind a single electron hole [$\text{Si}-\text{O}^{\bullet}-\text{Al}$]. The reaction thus forms a single-occupied molecular orbital (SOMO) at one of the bridging lattice oxygen atoms connected to an aluminum atom. When NO is

reintroduced to the zeolite, the oxidized zeolite then quickly accepts an electron from NO to reform the surface NO^+ radical cation.

NO is a stable radical species, though it has a low ionization energy (I.E.) of 9.26 eV due to its unpaired electron located on an antibonding orbital, significantly increasing its susceptibility to ionization. NO^+ is strongly electrophilic with a reversible redox potential of $E^\circ = 1.28 \text{ V vs. SCE}$ [59]. Note that upon thermal dehydroxylation ($\sim 1,023 \text{ K}$) of high-silica zeolites, the formation of single electron vacancies at framework oxygen atoms has been proposed to occur for zeolites exposed to air at high temperatures [60]. Yun and Lobo [61] have found that such oxidized zeolite samples can easily extract an electron from naphthalene, (I.E. of 8.14 eV), through an electron-transfer reaction forming a naphthalene radical cation. Although the I.E. value of NO is higher than that for naphthalene, it is still low compared to most stable compounds. The zeolite oxidation process observed here is different in that it occurs at significantly lower temperatures compared to the commonly observed dehydroxylation of Brønsted acid sites, indicating that the presence of NO and O_2 in our system facilitates this oxidation chemistry. Chemistry involving NO is unique and complex because of nitric oxide's ability to change redox states through one-electron processes [62].

To date there have been few direct structural investigations to characterize the geometry of the NO^+ site in the zeolite framework. Using FTIR spectroscopy in conjunction with isotopic labeling techniques, Hadjiivanov et al. [58] showed that NO^+ is coordinated to lattice oxygen atoms at cationic positions ($\text{O}_{\text{lattice}}\text{-NO}^+$). The authors detected an IR band at 977 cm^{-1} , nearby to the theoretical vibration of $1,000 \text{ cm}^{-1}$ for this interaction, and also confirmed that gas-phase O_2 is not involved in the bond. A computational investigation by Pidko et al. [63] over NaX zeolite indicates that NO^+ coordinates to the zeolite via a single oxygen atom and not via multiple lattice

oxygen atoms. The weak O-O bond has a bond-dissociation-energy of $142.3 \text{ kJ mol}^{-1}$ and can be easily broken at low temperatures, suggesting that NO^+ may bond through an O-O interaction with the zeolite oxygen atom [64]. On the other hand, the unpaired electron of NO is likely to reside at the nitrogen atom, since oxygen has a high electron affinity, thus making the O-O bond structure less plausible.

Similar NO/O₂ co-adsorption experiments were conducted over the Na-SSZ-13 and siliceous CHA materials to identify any differences that arise in the IR spectra from the absence of Brønsted acid sites or framework aluminum atoms. NO^+ formation was observed to occur on Na-SSZ-13 under the same conditions tested for H-SSZ-13, as indicated by an IR band at $\sim 2160 \text{ cm}^{-1}$. The IR signal intensity of NO^+ formed over Na-SSZ-13 was much weaker compared to that over H-SSZ-13, suggesting that this species forms much more readily in the presence of Brønsted acid sites. In addition to the positive IR band for NO^+ , a negative band at 3695 cm^{-1} was observed. This band is attributed to hydroxyl groups located on Na^+ cations, based on the assignment by Sedlmair et al. [65] in their study of NO/O₂ co-adsorption on NaY.

Over siliceous CHA, NO^+ formation was not observed in the IR spectra. No acidic OH IR bands were observed because, as expected, the sample was nearly free of aluminum impurities that would have led to acid sites. In fact, no N_xO_y surface species were observed over siliceous CHA at the temperatures investigated ($T > 423 \text{ K}$) from exposure to NO/O₂/NO₂ gas mixtures. This result shows that framework aluminum atoms with charge-compensating cations are necessary for the development of NO^+ and that siliceous CHA has no suitable sites for the NO^+ species to coordinate. The absence of any adsorbed species on the catalyst at elevated temperatures ($T > 423 \text{ K}$) explains the inability of this material to effectively catalyze the reaction in this high-temperature regime. Based on these results, 423 K is the approximate

transition point at which the confinement effect responsible for the low-temperature catalytic activity of the zeolite materials is no longer able to increase oxidation reaction rates with respect to the gas phase reaction. Although the H-SSZ-13 and Na-SSZ-13 materials can catalyze, via a second mechanism (involving NO^+), NO oxidation above ~ 423 K, siliceous CHA cannot facilitate the formation of these species. The high-temperature activity is thus unique to zeolite materials containing framework aluminum atoms although it may be possible to form similar species over Fe^{III} -, Ga^{III} -containing zeolites and perhaps on other solid acids such as heteropolyacids or sulphated zirconia.

NO^+ was found in H-SSZ-13 up to 623 K in the presence of 1,000 ppm NO and 5% O_2 (see Figure S.8 in the Supporting Information). As the temperature increased, the intensity of the NO^+ IR band diminished. Temperatures above 623 K were not investigated because this is the thermal stability limit of the IR cell. Similar studies carried out over Na-SSZ-13 showed that NO^+ was also stable on this material throughout the same temperature range, although it was present in significantly lower concentrations (see Figure S.9 in the Supporting Information).

The effect of NO partial pressure (0-2,000 ppm NO + 5% O_2) on the intensity of the NO^+ signal (2185 cm^{-1}), as well as the concomitant decrease in the Brønsted acid site peak intensity (3610 cm^{-1}), was monitored at 523 K over H-SSZ-13 (Figure 5). A clear correlation exists between the growth of the NO^+ IR band and the disappearance of the Brønsted acid site IR band as the NO partial pressure increases. This observation is consistent with the premise that NO^+ is forming at the expense of zeolite Brønsted acid sites.

To determine whether NO^+ formation has a direct effect on NO oxidation reaction rates over H-SSZ-13, rates were measured at 523 K as a function of NO partial pressure (0-2,000 ppm

NO + 5% O₂) and separately the intensity of the NO⁺ absorption band was recorded under the same conditions using the *in-situ* IR cell. The oxidation rates and NO⁺ areas are plotted as a function of the inlet NO partial pressure in Figure 6 where we observe a linear correlation between the intensity of the NO⁺ IR signal and the NO oxidation rate as a function of inlet NO pressure, strongly suggesting that NO⁺ is involved in the reaction mechanism. Identical experiments carried out for Na-SSZ-13 indicated a similar correlation between the NO⁺ IR signal and NO oxidation rate (see Figure S.5 in the Supporting Information).

To understand the formation of NO⁺ and the conditions under which it is stable on H-SSZ-13, the NO⁺ signal was monitored as a function of time under different gas compositions at a temperature of 573 K using IR spectroscopy (Figure 7). Initially, flow of 1,000 ppm NO does not produce an IR signal for NO⁺ at 2185 cm⁻¹ but switching on O₂ leads to the observation of a NO⁺ signal that remains stable while the NO/O₂ gas mixture passes over the zeolite. Then, the O₂ is shut off while NO flow is maintained; the IR signal for NO⁺ diminishes to about half of its initial intensity but it does not disappear. This is different from when NO was first introduced to the catalyst, in which NO⁺ was not observed, and indicates that the zeolite acid sites have been altered to now form NO⁺ in the presence of NO. Feeds of NO and NO/O₂ mixtures were cycled to ensure that the results are consistent (the IR signal levels verify this expectation). Pure He gas was subsequently introduced, and the NO⁺ signal disappeared entirely within several minutes. 1,000 ppm NO was reintroduced at this point, and the NO⁺ IR signal reemerged to its previous level. This is again different from the initial properties because at the beginning the addition of NO to the sample did not produce the NO⁺ signal. Increasing the concentration of NO to 2,000 ppm resulted in a further increase in the NO⁺ IR signal strength, indicating that NO⁺ concentration is directly affected by the NO concentration in the gas phase and that the sites are

not saturated at 1,000 ppm. Additionally, in a separate experiment NO^+ was also observed under exposure to a gas stream of NO_2 (100-200 ppm), and its IR signal intensity was also proportional to the concentration of NO_2 (spectra not shown). At a higher concentration of NO_2 in the feed, additional surface species were observed to form at 473 K (see Figure S.15 in the Supporting Information). NO^+ was observed to replace the acid site, as indicated by a positive IR band at 2170 cm^{-1} and a negative band at 3613 cm^{-1} . A complex set of IR bands at lower wavenumbers was also observed; these absorption bands are attributable to other charged N_xO_y species but cannot be assigned with certainty. The band at 2004 cm^{-1} could be from NO_2^+ , which has been observed between $2000\text{--}2100\text{ cm}^{-1}$ on NaY upon exposure to NO_2 [66], although NO_2^+ also has a vibrational frequency of 2350 cm^{-1} [66], which was not observed here. The band at 1629 cm^{-1} likely derives from the *cis* isomer of nitrites, whose N=O stretching mode results in an absorption in the $1630\text{--}1600\text{ cm}^{-1}$ region [67], but it could also be due to chemisorbed water [67]. The band at 1227 cm^{-1} could be attributed to surface nitrites [68]. The band at 952 cm^{-1} can be assigned with certainty to the $\text{O}_{\text{lattice}}\text{--NO}^+$ bond [58]. Lastly, note that a negative band at 3740 cm^{-1} is also observed, indicating that NO^+ species may also form on internal or external silanol groups. This was not observed in the experiments with NO and O_2 .

The finding that oxidation of the zeolite acid site is possible at relatively low temperatures ($T < 623\text{ K}$) may be significant. This protocol (co-addition of NO/ O_2 followed by flushing with He) is experimentally simple and can be used for the investigation of the oxidized acid sites in future studies. Further study of the properties of these sites is outside the scope of this report.

3.5 High-temperature NO oxidation reaction mechanism over H-SSZ-13

Based on our investigation of the reaction kinetics and surface species present on H-SSZ-13, we propose that NO^+ is acting as a reactive intermediate in the high-temperature regime according to the series of reactions involving NO and illustrated in Scheme 1. The NO_x^+ species described in Scheme 1 are important ions in atmospheric chemistry [69, 70]. NO_3^+ is known to form from the reaction between NO^+ and O_2 , with Collisionally Activated Dissociation (CAD) spectra showing that the species has O_2 -NO connectivity as opposed to a trigonal NO_3^+ structure [71]. Additionally, computational studies have shown that the $\text{NO}^+\cdot\text{O}_2$ complex is the lowest energy form of NO_3^+ ; the enthalpy of formation for the $\text{NO}^+\cdot\text{O}_2$ complex has been estimated to be $231.2 \text{ kcal mol}^{-1}$ [72]. This large enthalpy value suggests that step (B) in Scheme 1 is a strongly endothermic reaction, and is likely to be the elementary step with the largest energy barrier in Scheme 1. The ionization energies (I.E.) of NO, NO_2 , and NO_3 are 9.26, 9.59, and 12.57 eV, respectively. These values show that NO^+ has the lowest energy of formation amongst the NO_x^+ species, and is therefore the most stable. NO_3 is a radical species with a high electron affinity that commonly exists as the nitrate anion (NO_3^-); the NO_3^+ species is infrequently encountered due to the large I.E. of NO_3 . The I.E. values suggest that a zeolite-adsorbed NO_2^+ will be lower in energy compared to NO_3^+ , but will be slightly higher in energy compared to NO^+ . Our IR spectroscopy results agree that NO^+ is more stable compared to NO_2^+ and NO_3^+ , since NO^+ was the only NO_x^+ species detected.

At this point, using the pseudo-equilibrium approximation in combination with our experimental results, we can suggest the step most likely to be the RDS in the proposed mechanism. Recall that the fractional coverage of NO^+ is much greater compared to that of the other NO_x^+ cations (NO_2^+ or NO_3^+ were not detected), indicating that NO^+ is more stable and can be identified as the most abundant reaction intermediate (MARI). Thus, the NO_2^+ and NO_3^+ that

form in the mechanism illustrated in Scheme 1 will react quickly, making it less likely that steps (C) and (D) are rate-determining. Allowing step (B) of Scheme 1 to be the RDS, and assuming that all other steps are equilibrated, the following rate expression (see Supporting Information for detailed derivation and list of assumptions) can be derived:

$$r_{NO_2} = \frac{k_{app.(P_{NO})(P_{O_2})}}{1+K_{1.eq.}(P_{NO})} \quad (12)$$

Eq. 12 shows that at low coverage of Z^-NO^+ , for which $K_{1.eq.}$ is $\ll 1$, the expression simplifies to $r \sim (P_{NO})(P_{O_2})$. At higher Z^-NO^+ coverages the rate expression is better approximated by $r \sim (P_{NO})^\alpha(P_{O_2})$, where $0 < \alpha < 1$. In section 3.3, we established that the measured reaction orders for NO and O₂ were both ~ 1 over H-SSZ-13 at 473 K. This analysis shows that under conditions of low Z^-NO^+ coverage, and where step (B) in Scheme 1 is the RDS, the measured reaction orders agree with the proposed reaction mechanism (Scheme 1).

Assuming steps (C) and (D) of Scheme 1 to be rate determining leads to the following rate expressions (equations 13 and 14, respectively):

$$r_{NO_2} = \frac{k_{app.(P_{NO})^2(P_{O_2})}}{1+K_{1.eq.}(P_{NO})} \quad (13)$$

$$r_{NO_2} = \frac{k_{app.(P_{NO})^2(P_{O_2})}}{(P_{NO_2})[1+K_{1.eq.}(P_{NO})]} \quad (14)$$

From equation 13, we can see that low coverages of Z^-NO^+ lead to a simplified rate expression $r \sim (P_{NO})^2(P_{O_2})$, which does not agree with the experimentally observed reaction order of ~ 1 for NO. At higher Z^-NO^+ coverages, the rate expression becomes $r \sim (P_{NO})^\alpha(P_{O_2})$ with $1 < \alpha < 2$, which, in the limit, agrees with the experimentally observed value of 1.02. Nonetheless, under

our reaction conditions NO^+ coverage is, with all likelihood, low, especially at the high end of the temperature range investigated (623 K) and thus, step C is unlikely to be rate limiting. If step (D) is the RDS, the rate expression (eq. 14) simplifies to $r \sim (P_{\text{NO}})^2 (P_{\text{O}_2}) (P_{\text{NO}_2})^{-1}$ for low coverages of Z^-NO^+ , which again is inconsistent with the experimentally observed reaction order for NO. At higher Z^-NO^+ coverages, the rate expression becomes $r \sim (P_{\text{NO}})^\alpha (P_{\text{O}_2}) (P_{\text{NO}_2})^{-1}$ with $1 < \alpha < 2$. As described above, under the reaction conditions investigated NO^+ coverage is likely to be low and thus step (D) is also not likely the RDS. Mechanistic studies using $^{18}\text{O}_2/^{16}\text{O}_2$ isotopic switching will be necessary to provide additional evidence validating the reaction mechanism proposed in Scheme 1, but these experiments are beyond the scope of this report.

Scheme 2 shows a *qualitative* energy diagram for the proposed reaction mechanism in Scheme 1, with step (B) as the RDS. As discussed earlier, NO_3^+ is higher in energy compared to the other adsorbed NO_x^+ species, and therefore step (B) will be strongly endothermic, as illustrated in Scheme 2. According to the Hammond postulate then, we can surmise that the activated complex for this step will closely resemble in structure and be nearer in energy to the NO_3^+ product rather than the reactants. The apparent activation energies that were determined experimentally reflect the energy barrier for step (B) and consist of three terms: (1) the heat of adsorption for the molecular physisorption of O_2 within the zeolite pores, (2) the heat of adsorption of NO on the oxidized zeolite site to yield NO^+ , and (3) the intrinsic activation energy of the reaction. The heat of adsorption of O_2 on zeolites should be $\sim 15\text{-}20 \text{ kJ mol}^{-1}$ [73-75]; we have assumed a value of 17 kJ mol^{-1} for our calculations over H-SSZ-13. Using the Van't Hoff equation and the data in Figure S.8 (see Supporting Information), we estimated the heat of adsorption term of NO on the oxidized zeolite site for H-SSZ-13 to be $-42.4 \text{ kJ mol}^{-1}$.

Accordingly, the intrinsic activation energy for step (B) over H-SSZ-13 was determined to be 99 kJ mol⁻¹, which is considerably greater than the measured activation energy of 40.8 kJ mol⁻¹ and shows that the heat of adsorption terms lead to a sizeable decrease in the reaction barrier for the catalytic reaction.

Since our analysis of the rate expressions shows that step (B) is likely the RDS, it is constructive to examine the components of the apparent rate constant in eq. 12 to understand the physical significance of the term. The mathematical derivation of eq. 12 (see Supporting Information) shows that the apparent rate constant, $k_{app.} = k_2 K_{0eq.} K_{1eq.}$, is the product of a reaction rate constant and two adsorption equilibrium constants of elementary steps. $K_{0eq.}$ represents the equilibrium constant for the molecular physisorption of O₂ within the zeolite pores, and is expected to be small since the heat of adsorption of O₂ in H-chabazites is low (~15-20 kJ mol⁻¹) and the concentration of O₂ inside the zeolite pores should be similar to the gas phase concentration. $K_{0eq.}$ was estimated to be 35.5 using the same standard state (1 mol m⁻³) in the gas phase and in the zeolite micropores, thus confirming that it is small and will not contribute significantly to the apparent rate constant. By defining the standard state as ideal gas 1 mol m⁻³_{pore}, ΔS for O₂ physisorption is equal to zero, since O₂ will behave as an ideal gas both in the gas phase and when it is physisorbed within the zeolite pores, and thus will not experience a loss in entropy.

$$K_{0eq.} = \exp\left(\frac{-\Delta H}{RT}\right) \exp\left(\frac{\Delta S}{R}\right) \quad (15)$$

$K_{1eq.}$ represents the equilibrium constant for the adsorption of NO at vacant zeolite sites (Z[•]) to form NO⁺; this process is exothermic, and our IR spectroscopy studies have confirmed that the amount of NO⁺ attached to the zeolite decreases with increasing temperature (see Figure S.8 in

the Supporting Information). Since the apparent rate constant $k_{app.}$ in eq. 12 was observed to increase with increasing temperature, it seems that $K_{1eq.}$ also contributes minimally to the temperature dependence of $k_{app.}$. Eq. 15 can be used again to estimate $K_{1eq.}$, but in this case ΔS will not equal zero, since a significant loss in entropy is expected when transitioning from mobile NO molecules in the gas phase to immobile NO^+ attached the zeolite acid site. Using the assumption that the translational entropy will dominate the entropic losses compared to the rotational and vibrational partition functions, the Sackur-Tetrode equation (eq. 16) can be used to estimate ΔS .

$$S_{trans.} = R \cdot \ln \left[\frac{e^{5/2} \cdot V}{N_A} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \quad (16)$$

$S_{trans.}$ for NO (g) was found to equal $132.7 \text{ kJ mol}^{-1}$, while $S_{trans.}$ for Z^-NO^+ was assumed to equal 0, since the NO^+ attached to the zeolite acid site is expected to have minimal translational movement; therefore, ΔS_{ads} for NO adsorption was estimated to be $-132.7 \text{ kJ mol}^{-1}$. With an experimentally determined ΔH_{ads} value of $-42.4 \text{ kJ mol}^{-1}$ for the adsorption of NO at the oxidized zeolite site (discussed earlier and calculated using the Van't Hoff equation), $K_{1eq.}$ was estimated to equal 8.56×10^{-4} . Therefore, the intrinsic rate constant k_2 for elementary step (B) must be the dominant term in $k_{app.}$. According to the principles of transition state theory, the reaction rate is proportional to the concentration of the activated complex, allowing the rate expression to be rewritten as follows (eq. 17).

$$r_{NO_2} = \frac{2k_B T}{h} [NO_3^+]^\ddagger \quad (17)$$

Assuming that step (B) is the RDS, the activated complex has an expected composition of $[NO_3^+]^\ddagger$. Since step (B) is an endothermic reaction, and recalling that the rate constants were

observed to scale in the order of H-SSZ-13 > H-ZSM-5 > H-BEA, we can infer that the ability of the zeolite to stabilize the NO_3^+ intermediate decreases as the zeolite pore size increases. Noting that $[\text{NO}_3^+]^\ddagger$ is in equilibrium with $Z^-\text{NO}^+$ and O_2 (ad.), eq. 17 can be expanded into a rate expression in terms of measurable quantities (eq. 18, see Supporting Information for derivation). To ensure consistent units, the rate in eq. 18 should be expressed as a turnover frequency (per Brønsted acid site).

$$r_{\text{NO}_2} = \frac{\frac{2k_B T}{h} K_B^\ddagger K_{0eq.} K_{1eq.} [\text{NO}][\text{O}_2] \left(\frac{1 \text{ mol NO}^+}{1 \text{ mol Al}} \right)}{\left(\frac{1 \text{ mol}}{1 \text{ m}^3} \right)^2} \quad (18)$$

As mentioned, k_2 is expected to be the dominant term of the apparent rate constant $k_{app.} = k_2 K_{0eq.} K_{1eq.}$ since the product of $K_{0eq.}$ and $K_{1eq.}$ is small and exothermic. Eq. 18 shows that $k_2 = \frac{2k_B T}{h} K_B^\ddagger$, where $K_B^\ddagger$ is given by eq. 19 and represents the equilibrium for step (B) in Eyring formalism for Schemes 1 and 2.

$$K_B^\ddagger = \frac{\left(\frac{[\text{NO}_3^+]^\ddagger}{\left(\frac{1 \text{ mol}}{\text{mol Al}} \right)} \right)}{\left(\frac{[\text{NO}^+]}{\left(\frac{1 \text{ mol}}{\text{mol Al}} \right)} \right) \left(\frac{[\text{O}_2]}{\left(\frac{1 \text{ mol}}{\text{m}^3_{\text{pore}}} \right)} \right)} \quad (19)$$

At this point, $K_B^\ddagger$ can be calculated because the apparent rate constant ($k_{app.} = \frac{2k_B T}{h} K_B^\ddagger K_{0eq.} K_{1eq.}$) was measured experimentally, and $K_{0eq.}$ and $K_{1eq.}$ were estimated earlier in this section. At 573 K, $k_{app.} = 9.22 \times 10^3 \text{ L mol Al}^{-1} \text{ s}^{-1}$ for H-SSZ-13; therefore $K_B^\ddagger$ was found to equal 1.27×10^{-8} , resulting in a value of $3.04 \times 10^5 \text{ L mol (mol Al)}^{-1} \text{ s}^{-1}$ for k_2 . The small value for $K_B^\ddagger$ confirms that the equilibrium for step (B) lies far towards $Z^-\text{NO}^+$ rather than $Z^-\text{NO}_3^+$, and is consistent with

our observation that NO^+ is the only reaction intermediate present within the zeolite pores in appreciable quantities. This value also suggests that a large energy barrier exists in order to form NO_3^+ . Comparing the values for the three components of the apparent rate constant ($k_2 = 3.04 \times 10^5 \text{ L mol Al}^{-1} \text{ s}^{-1}$, $K_{0eq.} = 35.5$, $K_{1eq.} = 8.56 \times 10^{-4}$), k_2 is seen to be several orders of magnitude larger than $K_{0eq.}$ and $K_{1eq.}$ and hence it dictates the behavior of the apparent rate constant.

The pre-exponential factors (k_0) for H-SSZ-13, H-ZSM-5, and H-BEA were presented in section 3.3 (Table 2), and can be related to the entropy of formation of the transition state ($\Delta S^\ddagger$) from the gas-phase reactants. $\Delta S^\ddagger$ becomes more negative and kinetically unfavorable as the pre-exponential factor decreases; that is, the transition state has a more rigid structure compared to the gas-phase reactants. This is expected because the reactants (NO and O_2) are gas molecules and the activated complex is bound to the acid site inside the zeolite pores. The values in Table 2 indicate that the calculated pre-exponential factors decrease as follows: $\text{H-BEA} > \text{H-ZSM-5} > \text{H-SSZ-13}$. This order follows the decreasing zeolite pore size. The modest entropic gains that result from increased pore size do not result in higher reactivity, confirming that the stabilization of the transition states is an enthalpy-controlled process that benefits from smaller zeolite pore size. For instance, H-BEA, the sample exhibiting the largest activation energy and pre-exponential factor, showed the lowest reaction rates. $\Delta S^\ddagger$ values were calculated for each zeolite framework according to eq. 20, which relates the entropy to the measured rate constant. $\Delta S^\ddagger$ values for H-BEA, H-ZSM-5, and H-SSZ-13 were found to equal -307.3 , -317.8 , and $-320.9 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The entropic losses are quite substantial and are greatest for H-SSZ-13. However,

the higher activity observed over H-SSZ-13 confirms that the $\Delta H^\ddagger$ term prevails over the entropic term^[1].

$$k_{app.} = 2\kappa \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(\frac{-(E_a - 2RT)}{RT}\right) \left[\frac{mol}{m_{gas}^3}\right]^{-2} \quad (20)$$

Further understanding of the enthalpic stabilization of transition states can be gained from examining heats of adsorption of gas species such as N₂ and CO₂ in these zeolite frameworks. It would be better to examine such data for NO; however, we were not able to find any reliable values in the open literature, and instead have used the widely reported data for N₂ and CO₂ (Table 5). Heats of adsorption increase as the pore size decreases but the magnitude of the change is much lower (~35%) than the observed differences in activation energy for the NO oxidation reaction. The data thus suggest that differences in the heat of adsorption of the NO₃⁺ surface intermediate (or more precisely, the transition state [NO₃⁺][‡] leading to NO₃⁺ formation) between the three zeolites do not completely explain the difference in magnitude in activation energy (Differences in activation energy are ~15 kJ mol⁻¹, and for adsorption they are just 5 kJ mol⁻¹) It could also be that the observed differences reflect the fact that N₂ and CO₂ are not charged and are thus not good models for [NO₃⁺][‡].

4. Conclusion

The results presented in this report together with the data reported in reference 33 show the occurrence of two reaction regimes for the oxidation of NO over H- and Na-zeolites: activity increases with decreasing temperature below 423 K, and activity increases with increasing temperature above 423 K. In the high temperature regime, our experiments show that the zeolite

^[1] Note that $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were also estimated using the Eyring equation, and the values were found to be in close agreement with those calculated using eq. 20 and the relation $E_a = \Delta H^\ddagger + mRT$.

framework (CHA, BEA, MFI) has a substantial effect on NO oxidation rates, with activity being inversely proportional to the zeolite pore size. Activation energies scale in the order of CHA < MFI < BEA, and application of transition state theory shows that the smaller pores provide significantly greater enthalpic stabilization for the activated complex that more than compensate for the larger entropic costs. Siliceous samples show little activity at elevated temperatures (> 423 K), indicating that the confinement effect responsible for activity in the low-temperature regime is no longer substantial and that framework aluminum atoms are required for NO oxidation activity above 423 K [32, 33]. A change in the reaction mechanism at ~423 K is deduced by a change in activation energy and the reaction orders: rates are second order in NO at low temperature [32, 33], but first order in NO at high temperature. *In-situ* FTIR studies reveal that NO^+ is the only observable N_xO_y species present in significant concentrations on the aluminosilicate zeolites at high temperatures, and we have proposed plausible mechanisms for the formation of NO^+ at framework aluminum positions within the zeolite pores. We also show that NO^+ is in equilibrium with gas phase NO, and desorbs (as NO) leaving behind an oxidized acid site ($\text{Si-O}\bullet\text{-Al}$). We have identified oxidizing conditions that yield this new site, allowing future studies to examine its potential role in other reactions. We have shown that NO oxidation activity is directly proportional to the amount of NO^+ present, and have confirmed that siliceous samples are unable to form NO^+ or any other surface species above 423 K (within the limits of detection of the IR method). Finally, we have proposed a mechanism for the high-temperature NO oxidation reaction over H-SSZ-13, and have identified the most probable RDS that is consistent with the observed reaction orders and observed reaction intermediates. Finally, note that the activities displayed by all of the materials in this report were observed under dry conditions; it is very likely that the presence of water would significantly diminish their catalytic

properties for NO oxidation, since NO^+ can react with water and produce nitrous acid. The results from this investigation suggest that other solid acid catalysts, such as metal oxides over alumina or acidic polyoxometallates, may be capable of catalyzing the NO oxidation reaction by similar mechanisms. The results from this work may also have significance in the NH_3 -SCR NO_x mechanism over zeolites, although the measured TOFs for NO oxidation appear to be considerably lower than those seen for NH_3 -SCR.

Author Contributions

JAL conducted the experiments, analyzed results and co-wrote the manuscript. RFL supervised the research and co-wrote the manuscript.

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Supporting Information

Figures and tables provide additional experimental results pertaining to materials characterization, reaction rates, kinetics, IR surface spectroscopy, and derivation of rate expressions for the high-temperature NO oxidation reaction mechanism over H-SSZ-13.

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Figure Captions

Figure 1. Arrhenius plots of the forward NO oxidation rates (1,000 ppm NO + 5% O₂, 100 sccm, 0.1 g catalyst) at 298-623 K over SSZ-13 (CHA) materials.

Figure 2. NO oxidation turn-over-frequencies (TOFs) per Brønsted acid site over H-SSZ-13, H-ZSM-5, and H-BEA with varying Si/Al ratios (T = 423-623 K).

Figure 3. NO Oxidation Rate over H-SSZ-13 (Si/Al = 12) at 473 K versus NO (200-1,000 ppm) + 5% O₂ (●), O₂ (1-5%) + 500 ppm NO (■), and NO₂ (50-500 ppm) + 500 ppm NO + 5% O₂ (▲).

Figure 4. IR spectra obtained over H-SSZ-13 at 573 K showing formation of NO⁺ (2185 cm⁻¹) and disappearance of Brønsted acid sites (3610 cm⁻¹).

Figure 5. Correlation between NO⁺ IR band and Brønsted acid site IR band over H-SSZ-13 at 523 K.

Figure 6. Correlation between measured NO oxidation rate and formation of NO⁺ IR signal peak area over H-SSZ-13 at 523 K (500-2,000 ppm NO + 5% O₂).

Figure 7. Area of the NO⁺ IR signal (2185 cm⁻¹) monitored as a function of time for various inlet gas compositions (He, 1,000 ppm NO, 2,000 ppm NO, 1,000 ppm NO + 5% O₂) over H-SSZ-13 at 573 K.

Table Captions

Table 1. Microporous volumes, external surface areas, and estimated Si/Al ratios for H-SSZ-13, H-ZSM-5, and H-BEA materials.

Table 2. Measured NO oxidation rates and turn-over-frequencies ($T = 473$ K), and calculated activation energies (E_a) and pre-exponential factors (k_o) ($T = 423$ - 623 K) for H-SSZ-13 (Si/Al = 12), H-ZSM-5 (Si/Al = 12), and H-BEA (Si/Al = 12.5).

Table 3. Activation energies for NO oxidation over zeolite materials reported in the literature.

Table 4. Average NO oxidation turn-over-frequencies ($T = 473$ K) and calculated activation energies (E_a) and pre-exponential factors (k_o) ($T = 423$ - 623 K) for H-SSZ-13, H-ZSM-5, and H-BEA.

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Table 1. Microporous volumes, external surface areas, and estimated Si/Al ratios for H-SSZ-13, H-ZSM-5, and H-BEA materials.

Material	Microporous Volume [cm³ g⁻¹]	External Surface Area [m² g⁻¹]	Si/Al Ratio
H-SSZ-13	0.28	32	6.4
H-SSZ-13	0.27	32	11.8
H-ZSM-5	0.12	100	12.1
H-ZSM-5	0.12	102	18.3
H-BEA	0.17	162	12.7
H-BEA	0.18	165	18.7

Table 2. Measured NO oxidation rates and turn-over-frequencies ($T = 473$ K), and calculated activation energies (E_a) and pre-exponential factors (k_0) ($T = 423$ - 623 K) for H-SSZ-13 (Si/Al = 12), H-ZSM-5 (Si/Al = 12), and H-BEA (Si/Al = 12.5).

Material	Rate	E_a	k_0	TOF
	[mol s ⁻¹ g _{cat.} ⁻¹]	[kJ mol ⁻¹]	[L ² mol ⁻¹ s ⁻¹]	[s ⁻¹]
H-SSZ-13	6.12×10^{-8}	39.6	3.44×10^3	6.74×10^{-5}
H-ZSM-5	2.09×10^{-8}	45.1	9.58×10^3	2.32×10^{-5}
H-BEA	8.21×10^{-9}	54.2	2.78×10^4	9.35×10^{-6}

Table 3. Activation energies for NO oxidation over zeolite materials reported in the literature.

Material	E_a
	[kJ mol ⁻¹]
Cu-SSZ-13	57.6 [15]
Cu-SSZ-13	52.5 [17]
Commercial SCR Cu-zeolite	29-31 [45]
Commercial SCR Cu-zeolite	32 [46]
Cu-ZSM-5	8.9 [47]
Fe-ZSM-5	39-43.2 [48-50]
Fe-MFI	43.1 [49]
Cu-MFI	75.3 [49]
Fe-FER	59.7 [50]
H-MOR	46 [13]
H-MOR	21 [13]
Pt/Al ₂ O ₃	39 [51]

Table 4. Average NO oxidation turn-over-frequencies ($T = 473$ K) and calculated activation energies (E_a) and pre-exponential factors (k_o) ($T = 423$ - 623 K) for H-SSZ-13, H-ZSM-5, and H-BEA.

Material	TOF [s ⁻¹]	E_a [kJ mol ⁻¹]	k_o [L ² mol ⁻¹ s ⁻¹]
H-SSZ-13	$4.72 \times 10^{-5} \pm 0.071 \times 10^{-5}$	40.8 ± 1.1	$3.53 \times 10^3 \pm 0.15 \times 10^3$
H-ZSM-5	$2.21 \times 10^{-5} \pm 0.26 \times 10^{-5}$	45.7 ± 2.6	$7.05 \times 10^3 \pm 3.4 \times 10^3$
H-BEA	$1.02 \times 10^{-5} \pm 0.11 \times 10^{-5}$	55.5 ± 1.8	$2.86 \times 10^4 \pm 0.13 \times 10^4$

Table 5. Isosteric heats of adsorption ($Q_{\text{st.}}$) of N_2 and CO_2 over selected zeolite structures.

Material	$Q_{\text{st.}}$	$Q_{\text{st.}}$
	[kJ mol ⁻¹] CO_2	[kJ mol ⁻¹] N_2
BEA (siliceous)	18.6 [76]	11.2 [76]
MFI (siliceous)	24.2 [76]	16.2 [76]
CHA (siliceous)	23.0 [76]	13.6 [76]
H-BEA (Si/Al =20)	33.0 [77]	19.0 [77]
H-ZSM-5 (Si/Al =30)	38.0 [78]	20.7 [78]
H-SSZ-13 (Si/Al =6, 80)	35.2 [79]	19.3 [80]

Scheme 1. Proposed NO oxidation reaction mechanism over H-SSZ-13 in the high-temperature regime ($T > 423$ K). In this sequence $Z\cdot$ represents the oxidized zeolite acid site.

Scheme 2. Qualitative energy diagram for the proposed NO oxidation reaction mechanism over H-SSZ-13, assuming step (B) as the RDS.

Graphical abstract