Biomimetic CO oxidation below – 100 °C by a nitrate-containing metal-free microporous system

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Short title: First example of biomimetic CO oxidation with a nitrate at -140 °C by a solid non-metal containing microporous system.

Abstract: CO oxidation is of importance both for organic and inorganic systems. Transition and precious metals on various supports can oxidize CO to CO2. Among them, few systems, like Au/TiO2, can perform CO oxidation at the low temperature of -70 °C. Living (an)aerobic organisms perform CO oxidation with nitrate using complex enzymes under ambient temperatures which is an important pathway of their living cycle that enables them to “breathe”/produce energy in the absence of oxygen and leads to the carbonate mineral formation. Herein, we report that CO can be oxidized to CO2 by nitrate at –140 °C in completely inorganic system (zeolite) without metals. The transformation of NOx and CO species in zeolite as well as the origin of this unique activity (catalyzed by Bronsted acid sites) are clarified using spectroscopic and computational approach.

One Sentence Summary: Discovery of biomimetic CO oxidation pathway by nitrate in an inorganic non-metal system.
CO oxidation is important both for automotive emissions control and in living microorganisms [1-8]. More specifically, inorganic materials such as transition/noble metals on solid supports are capable of oxidizing CO at elevated temperatures [1,2]. Among such systems, Au nanoparticles supported on titania, discovered by Haruta, represents a material active for CO oxidation at the lowest known temperature of -70 °C [1]. In anaerobic and aerobic microorganisms, enzymes evolved to oxidize CO to CO₂ by nitrate as shown in the pioneering studies of King and co-workers [3-5,8]. The energy produced is used to sustain life while emitted CO₂ leads to formation of carbonate minerals, for example [3-7]. Moreover, search for carbonate minerals/CO₂ on other planets (Mars) is ongoing to possibly confirm whether anaerobic life was ever present on such planets [5,8].

We discovered a pathway of CO oxidation by nitrate in a completely inorganic, non-metal crystalline system at -140 °C, more specifically zeolite SSZ-13. First, we had to clarify the chemistry of NOₓ species in zeolite under different conditions. In the 1980s, it was first discovered that NO⁺ species can form in Na-zeolites upon interaction with (NO+O₂) or NO₂ using Raman and infra-red spectroscopy [9]. Later on, K. Hadjiivanov and co-workers’ pioneering studies [10-12] allowed to establish, using FTIR spectroscopy and isotopic methods on NₓOᵧ molecules, that NO⁺ can indeed form in ZSM-5 upon interaction with (NO+O₂) mixture. NO₂ was shown to disproportionate to NO⁺ and NO₃⁻ in the zeolites in Li/K/Na forms as well [8]. Although it was clear that NO⁺ can be produced in zeolites from NO+O₂ mixtures and specific mechanisms were proposed, we investigated its production and chemical properties using spectroscopy and density functional theory calculations.

We started by introducing NO₂ onto small pore H-SSZ-13 zeolites with Si/Al ratios 12 and 6. SSZ-13 zeolite was chosen because it is the one often encountered in nature [13], it is a robust, hydrothermally stable framework used extensively in catalytic aftertreatment systems to decrease automotive pollution [14-17]. Additionally, it is the framework with only one equivalent framework T site [15] which is more straightforward to model than frameworks with broad distribution and location of T-sites. Fig.1 A depicts in-situ FTIR data during sequential adsorption of NO₂ on H-SSZ-13 with Si/Al ~ 12 at 25 °C. Surprisingly, despite the fact that NO₂ interaction with Na/K/Li forms of zeolites has been studied, few studies have been reported for NO₂ interaction with H-form of zeolites and none for SSZ-13. During adsorption of nitrogen dioxide two bands develop simultaneously in the N-O stretching region: one with a maximum at ~2171
cm\(^{-1}\) (belonging to NO\(^+\)) and one with a maximum at \(~1650\) cm\(^{-1}\) (belonging to free HNO\(_3\)). This corresponds to disproportionation reaction of NO\(_2\) to NO and HNO\(_3\): \(2\text{NO}_2 + \text{H-zeolite} \rightarrow \text{Zeolite-NO}^+ + \text{HNO}_3\)

Indeed, NO\(_2\) is known to be easily dimerizable to N\(_2\)O\(_4\) which, in highly polar solvents (such as ethylacetate, for example) or in the highly polar zeolitic micropores favors disproportionation to [NO\(^+\)][NO\(_3\)^-], which can react with zeolite protons (acid denoted as H-zeolite) in a scheme depicted above.

![Fig. 1. A. In-situ FTIR NO stretching region during sequential NO\(_2\) adsorption (2 Torr) on H-SSZ-13 with Si/Al ~ 12. B. OH stretching region during process in described in A. C. Adsorption of excess NO\(_2\) (2 Torr) on NO\(_2\)-saturated sample in A.](image)

The band representing NO\(^+\) is not symmetrical and it corresponds to two NO\(^+\) stretches at \(~2195\) and \(~2171\) cm\(^{-1}\). Concomitant to the development of these two absorption bands is the gradual intensity decrease of the two OH stretching features at 3612 and 3585 cm\(^{-1}\) (Fig. 2B). Thus, NO\(^+\) replaces protons near at least two distinct Al atom environments. Concurrently, a new OH stretching band appears at 3667 cm\(^{-1}\), corresponding the OH stretch of nitric acid. Thus, NO\(_2\) reacts with zeolite to form NO\(^+\) near the framework oxygens (in place of acidic protons) and HNO\(_3\).

Similar chemistry is observed for H-SSZ-13 with a different Si/Al ratio ~ 6 with slightly different distribution with NO\(^+\) species formed (see difference spectra in SI Fig. S1, HAADF-STEM images of SSZ-13 crystals are shown in Fig. S2). This is fully consistent with the DFT calculations, which show that the reaction: \(\text{Zeo/H}^+ + 2\times\text{NO}_2(g) \rightarrow \text{Zeo/NO}^+ + \text{HNO}_3(g)\) is exothermic by \(-46\) kJ/mol. Conceptually, NO\(^+\) can bind with an X\(^-\) anion in two fundamentally different ways to form NOX complexes. 1). [N≡O]\(^+\) complexes with weakly coordinating anions, like BF\(_4\)-. In these complexes
NO\(^+\) behaves as a free (or semi-free) cation exhibiting an N-O stretching vibrational frequency of \(\geq 2,300\ \text{cm}^{-1}\), for example 2340 cm\(^{-1}\) in NO[BF\(_4\)], 2326 cm\(^{-1}\) in NO[AuF\(_6\)], and 2298 cm\(^{-1}\) in concentrated sulfuric acid solutions for free [NO]\(^+\) [20]. NO\(^+\) forms complexes with X- but a covalent bond between N and X (X is most often a halogen) is preserved: in this case a bent O=N-X molecule forms with an O-N-X angle <180\(^\circ\). Complexes like these exhibit N-O vibrational frequencies between 1,950 and 1,800 cm\(^{-1}\) [21]. Furthermore, even for non-halogens the bent non-ionic M-N=O moieties with fully covalent N-M bonds and bent Metal-N-O angle (120<angle<180) show \(\nu_{\text{NO}}<1,900\ \text{cm}^{-1}\) in the IR spectra [22]. DFT calculations for free NO\(^+\) and NO\(_X\) complexes are in good agreement with the experimental trend (Table S1). However, for the NO\(^+\) in zeolite we observe \(\nu_{\text{NO}}\) in the intermediate region between 2,300 and 1,950 (but closer to the former). This does indeed suggest that NO\(^+\) and O-Zeolite interaction has a significant covalent character (i.e., NO\(^+\) is not a free-floating ion in zeolite). Further confirmation of this is the observation of the same FWHM of NO\(^+\) band upon warming NO\(^+\)/SSZ-13 system from 77 to 298 K (the NO\(^+\) band FWHM does not change, Fig. S3) suggesting that NO\(^+\) structure is attached to the zeolite and remains stable with temperature change (no shifting or broadening upon significant temperature changes). Unlike the 2133 cm\(^{-1}\) NO\(^+\) band in ZSM-5 [11], the NO\(^+\) bands in SSZ-13 are located at higher wavenumbers (at \(\sim 2170\) and 2200 cm\(^{-1}\)) and are characterized by higher thermal stability up to 200 \(^\circ\)C under high vacuum (Fig. S4) in contrast to NO\(^+\) in H/ZSM-5 located at 2133 cm\(^{-1}\) and which starts desorbing above room temperature.

Adsorption of excess NO\(_2\) on NO\(^+\)/zeolite with Si/Al \(~\) 6 (Fig. S5) and 12 (Fig. 1C) leads to the decrease of the intensity of the NO\(^+\) stretching band in the expense of a new NO band at \(\sim 2230\ \text{cm}^{-1}\) (lying higher than the original NO\(^+\) bands by \(\sim 35\) and \(\sim 58\ \text{cm}^{-1}\) correspondingly). Simultaneously, two new vibrational features appear; a sharp band at \(\sim 1740\ \text{cm}^{-1}\) and a shoulder at \(\sim 2080\ \text{cm}^{-1}\) (clearly seen in the difference spectra and spectra upon evacuation, Fig. S5, S8) as the excess NO\(_2\) produces an NO\(^+\)-NO\(_2\) complex. The formation of such a complex has been suggested, on the basis of Rietveld refinement of synchrotron XRD data, for NO\(^+\) interacting with excess NO\(_2\) in the supercages of Ba-FAU zeolite [19]. The onset of the formation of this complex coincides with the appearance of the band at 1746 cm\(^{-1}\) [18]. DFT calculations (Fig. S10) show the N-O stretches of NO\(^+\)-NO\(_2\) complex lie at \(\sim 2042\) and 1722 cm\(^{-1}\). Considering the systematic shift of calculated DFT NO stretches relative to experimental values by 20-30 cm\(^{-1}\) (due to the non-
innocent nature of NO adsorption, unlike in the CO case) this agrees well with ~2080 and ~1746 cm\(^{-1}\) bands for the NO\(^+\)-NO\(_2\) complex. The nature of the 2,230 cm\(^{-1}\) band is discussed below.

The chemistry we observe when reacting a mixture of NO+O\(_2\) over H-zeolites is somewhat different from the case discussed above for NO\(_2\). It was shown in the 1980s that NO+O\(_2\) in microporous materials can easily produce NO\(_2\) \cite{25}. The thus formed NO\(_2\), in turn, can either dimerize to form N\(_2\)O\(_4\) or react with NO to form N\(_2\)O\(_3\). Due to the presence of excess NO in the system the primary reaction is N\(_2\)O\(_3\) formation. The thus formed N\(_2\)O\(_3\) can disproportionate to the ion pair NO\(^+\)NO\(_2^-\) that, in turn, can react with a zeolitic proton. Indeed, when we mix NO with sub-stoichiometric amounts on oxygen, we see the immediate appearance of the IR bands characteristic of both NO\(^+\) (2174 cm\(^{-1}\)) and N\(_2\)O\(_3\) (1570 and 1970 cm\(^{-1}\)) (Fig. S6). The intensities of the IR bands of N\(_2\)O\(_3\) initially grow rapidly, and then, after reaching their maxima, they begin to lose their intensities. The IR feature of adsorbed NO\(^+\) continuously grows during the entire experiment (Fig. S6) while Bronsted acidic protons are consumed:

\[
\begin{align*}
\text{N}_2\text{O}_3 &\leftrightarrow \text{NO}^+\text{NO}_2^- \\
\text{NO}^+\text{NO}_2^- + \text{zeolite-H}^+ &\rightarrow \text{NO}^+\text{-zeolite} + \text{HNO}_2
\end{align*}
\]

HNO\(_2\) then quickly reacts with H\(^+\) to form NO\(^+\) and H\(_2\)O. The major difference between the two NO\(^+\) formation processes (NO\(_2\) vs. NO+O\(_2\)) is the production of nitrates in the NO\(_2\) only process, and the formation of H\(_2\)O in the NO+O\(_2\) reaction. NO\(^+\), formed in either processes, is stable under vacuum at 77 K and only desorbs above 150 \(^\circ\)C under high vacuum. Furthermore, the chemistry of NO\(^+\) confined in zeolite is peculiar. Adsorption of NO\(_2\) at room temperature leads to the formation of NO\(^+\)-NO\(_2\) complex as well as a shift of the NO\(^+\) band to 2230 cm\(^{-1}\). Evacuation restores the IR signature of the original NO\(^+\) as the [NO\(^+\)-NO\(_2\)] complex decomposes (Figs. S7 and S8). Adsorption of CO at low temperature (77 K) on the NO\(^+\)/H/SSZ-13 shows the production of an NO\(^+\)-CO complex evidenced by the blue shift of the NO\(^+\) vibrational signature to ~2220 cm\(^{-1}\) \textit{(vide infra)} (Fig. 3A). In contrast, upon the adsorption of NO on the NO\(^+\)/H/SSZ-13 sample at 77 K the IR band of NO\(^+\) redshifts to 2013 cm\(^{-1}\) evidencing the selective production of the NO\(^+\)-NO complex.

Thus, this novel chemistry provides a hitherto unknown insight how adsorption of an adsorbate (NO, CO, NO\(_2\)) changes the properties of the cation with which it interacts. Normally, such cations are metal cations that have no corresponding IR active vibrations, and the information regarding the changes incurred during adsorption is hidden.
In-situ FTIR during sequential CO adsorption (2 Torr) at 100 K on H-SSZ-13 with Si/Al ~ 12 that was previously reacted with NO₂ at RT to form NO⁺ and NO₃⁻. Excess of NO₂ was removed by vacuuming at 10⁻⁶ Torr at RT. B. In-situ FTIR during sequential NO adsorption (2 Torr) at 100 K on H-SSZ-13 with Si/Al ~ 12 that was previously reacted with NO₂ at RT. Excess of NO₂ was removed by vacuuming at 10⁻⁶ Torr at RT. C. In-situ FTIR during 10⁻⁷ Torr vacuum applied after B at 100 K. NO leaves Zeo-NO⁺-NO complex under vacuum, restoring NO⁺.

In our case, however, because NO⁺ itself has an active N-O vibration, we see that adsorption of CO, NO and NO₂ shifts its electronic signature, our DFT calculations showed that the interaction between NO⁺ and CO or NO₂ is relatively weak with a binding energy of the adsorbed molecule below -20 kJ/mol in absolute value (Table S1). Hence, we conclude that since the concentration of CO or NO₂ is high in the zeolite pores, these gas phase molecules slightly shift NO⁺ further from its equilibrium position in the zeolite. This, in turn, weakens the interaction between NO⁺ and zeolite, leading to a shortening in the N-O distance and a blue shift of N-O vibrational
frequency to ~2230 cm\(^{-1}\) (in the case of NO\(_2\)) and 2220 cm\(^{-1}\) (in the case of CO). This provides a unique insight into the interaction of extra-framework cations with adsorbates, not routinely available even from the most sophisticated synchrotron XRD and Rietveld refinement methods. However, in the case of NO, the shift is to a significantly lower frequency. This finding can be rationalized by our DFT results, since in this case a stable Zeo/NO\(^+\)-NO complex is formed (Fig. S10) in the zeolite with a binding energy of NO to Zeo/NO\(^+\) of -52 kJ/mol (Table S1). This structure has two frequencies at 2009 and 1911 cm\(^{-1}\). They can rationalize the experimental bands at 2013 and 1871 cm\(^{-1}\). In addition, calculated ONNO species in gas phase has frequencies at 1879 and 1727 cm\(^{-1}\). Thus, they can rationalize the experimental bands at 1870 and 1685 cm\(^{-1}\).

In-situ heating of the NO-CO complex produced from N\(_2\)O\(_3\) reaction with H-SSZ-13 leads to no CO\(_2\) formation (Fig. S9). However, when the NO\(^+\)/SSZ-13 sample prepared by the disproportionation of NO\(_2\) (i.e., contained large amounts of nitrates) was heated from -170 to -140 °C in the presence of CO, the immediate formation of CO\(_2\) inside the zeolite micropores was observed, evidenced by the appearance of a sharp band at 2345 cm\(^{-1}\) characteristic signature of adsorbed CO\(_2\) [23]. CO was oxidized by nitrates: as the intensity of the characteristic vibrational feature of adsorbed CO\(_2\) gradually increased, the intensity of the 1645 cm\(^{-1}\) nitrate band simultaneously decreased. These results unambiguously show that CO can be oxidized by nitrates in this zeolite at the very low temperature of -140 °C (Fig. 3).
In-situ FTIR during increase of temperature from 100 K (red line, described in Fig. 2A) to 135 K (at this temperature CO₂ starts to evolve and we hold at this T until CO₂ reaches maximum level in ~ 2 minutes). The inset shows the magnified CO₂ region. Note that we collected spectra at temperatures intermediate between 100 and 135 K, and no CO₂ formation was detected until 135 K.

This biomimetic chemistry by a completely inorganic non-metal system occurs at temperatures previously unseen for such a conversion. Moreover, when we react CO with NO₃⁻ at room temperature (in the same system), no reaction takes place at all! How can this seemingly puzzling fact be rationalized? It is well-known the catalysis can occur when the reacting molecule is adsorbed/chemisorbed. In the case of CO, at room temperature CO is not adsorbed by the Bronsted acid protons of -Si-OH-Al groups, as evidenced by the lack of CO stretches other than gas-phase CO. However, CO interacts with Bronsted acid protons of the zeolite at lower temperatures forming -H⁺---CO complex [25]. IR CO stretching feature in this complex is centered at ~2175 cm⁻¹ [25]. The major consequence of the binding of CO to H⁺ is the polarization of the C-O bond as C(δ⁺)-O(δ⁻) because in the H⁺-CO complex no backdonation from the proton to CO is present, and only electrostatic interaction and formation of a sigma bond takes place with charge transfer from C to H⁺. This polarization (i.e., formation of C(δ⁺)-O(δ⁻)) makes CO susceptible to nucleophilic...
attack by NO$_3^-$ to form CO$_2$ and reduced NOx species. DFT calculations further support the proposed route. We considered four mechanisms for CO oxidation by HNO$_3$ in H-CHA. They are presented schematically in Fig. 4, as well as the corresponding energetic diagrams.

**Mechanism A**

\[
\begin{align*}
\text{Zeo1} + \text{HNO}_3 + \text{CO} & \rightarrow \text{Zeo1/CO/HNO}_3 \rightarrow [\text{TS1}]^# \rightarrow \text{Zeo1/CO}_2/\text{HNO}_2 \\
\end{align*}
\]

**Mechanism B**

\[
\begin{align*}
\text{Zeo1/CO/HNO}_3 & \rightarrow [\text{TS2}]^# \rightarrow \text{Zeo1/CO}_2/\text{HNO}_2 \\
\text{Zeo1/CO/HNO}_3 & \rightarrow [\text{TS2}]^# \rightarrow \text{Zeo2/NO}_2^+/\text{HCO}_2^- \\
\end{align*}
\]

**Mechanism C**

\[
\begin{align*}
[\text{TS2}]^# & \rightarrow \text{Zeo1/CO}_2/\text{HNO}_2 \\
\end{align*}
\]
Fig. 4. Mechanisms A, B, C, and D of CO oxidation by HNO$_3$ in H-CHA. Zeolite structures Zeo1 and Zeo2 differ by the different location of the zeolite proton at basic O centers from AlO$_4$ unit. The first species given after Zeo1 and Zeo2 are the one which interacts with the zeolite proton. Corresponding energy diagrams of the investigated mechanisms (Mechanisms A, B, C, and D) for CO oxidation by HNO$_3$ in H-CHA. The corresponding structures are also shown. Shorter names are used for the structures in the energy diagrams with respect to the schemes.

All mechanisms start with the adsorption of the reactants, CO and HNO3, via hydrogen bonds to the bridging OH group and basic zeolite oxygen center, respectively. In this initial state (IS) structure (Zeo1/CO/HNO3) the C-O vibrational frequency was calculated to be 2175 cm\(^{-1}\), in line with the corresponding experimental band. Mechanisms A and B are one-step mechanisms. In the former one the CO molecule is oxidized by the HNO3 via transition state structure TS1 with no direct participation of the zeolite. In mechanism B, the CO molecule is oxidized to CO2 via transition state structure TS2, where zeolite participates actively in the process via movement of the proton from the bridging OH group towards C atom from the CO molecule and via the basic zeolite oxygen, which attracts the nitric acid’s proton. TS2 structure seems to correspond to a bifurcation point, since it may be decomposed in two ways (i) directly to CO2 and HNO2 via the electron transfer shown by the arrows in the mechanism B; and (ii) to formation of a complex HCOO\(^{-}\)NO2\(^{+}\) (IC) as the zeolite proton interacts with an O center from NO2\(^{+}\), as shown in mechanism C. From the latter intermediate can be formed the final products (CO2 and HNO2) via the same TS2 structure (Mechanism C). Alternatively, if the intermediate is coordinated to the zeolite (see Zeol2/HCO2-/NO2+, ID) CO2 and HNO2 can be formed via TS3, which includes a H\(^{-}\) transfer from HCOO\(^{-}\) to NO2\(^{+}\) (Mechanism D). In all mechanisms considered the CO oxidation was calculated to be exothermic by 187 to 217 kJ/mol, depending on the coordination of the products (Figure 4), thus we investigated only kinetic aspects in depth. Energy diagrams show that the most plausible are Mechanisms B and C with a barrier of the rate limiting steps (which are the same) of 81 kJ/mol. In addition, we calculated the Gibbs free energy barriers of this rate limiting step of both mechanisms at 140 K to be 58 kJ/mol. Since these steps are the first ones, formation of an intermediate is not expected in line with our experimental results. Both mechanisms involve the direct participation of the zeolite via H\(^{+}\) transfers and as well as the formation of initial complex of CO to the zeolite H\(^{+}\) is crucial for the oxidation process. The calculated energy barriers for the rate limiting steps of mechanisms A and D are notably higher (Figure 4).

We also considered CO oxidation on Zeol/NO2\(^{+}\) (Fig. S11), in which NO2\(^{+}\) are the charge-compensating species of the negatively charged zeolite framework, forming kind of nitrate with
the O center from the zeolite. The calculated IR frequencies of such Zeo/NO$_2^+$ species are 2046 and 1358 cm$^{-1}$ and move to 2055 and 1353 cm$^{-1}$ after CO adsorption. However, the barrier for the reaction: Zeo/NO$_2^+$ + CO $\rightarrow$ Zeo/NO$^+$ + CO$_2$ is very high, 143 kJ/mol, thus the role of NO$_2^+$ species as a CO oxidizing agent can be discarded.

In summary, we discovered that CO can be oxidized to CO$_2$ by nitrate in zeolite micropores at temperatures as low as -140 °C. This reaction was previously known to be catalyzed by complex enzyme molecules in living (an) aerobic organisms. However, no noble (or other) metal systems have been known that can perform this biologically important reaction under mild conditions. Remarkably, fully inorganic system with no (noble) metals performs such a reaction at -140 °C.

Interaction of CO with Bronsted acid protons in confined nanopore produces -H$^+$-CO complex making the carbon atoms susceptible for nucleophilic attack by a nitrate, revealing a hitherto unknown pathway for CO conversion chemistry in inorganic systems at low temperatures.

References and notes

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Competing interests: Authors declare no competing interests.

Data and materials availability: All data is available in the main text or the supplementary materials.
Supplementary Materials:

Materials and Methods
H-SSZ-13 was synthesized using previously described methods [14,16 in the main text]. More specifically, a Na-form of SSZ-13 with Si/Al ratio ~6 and 10-12 were prepared, and then exchanged three times with 2 M ammonium nitrate solution at 80 °C. The powder was purified by consecutive centrifugation cycles after washing with DI. The wet powder was dried at 100 °C, and then calcined at 550 °C for 5 hours in the flow of dry air. All the chemicals used were the highest-grade purity available.

The in situ static transmission IR experiments were conducted in a home-built cell housed in the sample compartment of a Bruker Vertex 80 spectrometer, equipped with an MCT detector and operated at 4 cm⁻¹ resolution. The powder sample was pressed onto a tungsten mesh which, in turn, was mounted onto a copper heating assembly attached to a ceramic feedthrough. The sample could be resistively heated, and the sample temperature was monitored by a thermocouple spot welded onto the top center of the W grid. The cold finger on the glass bulb containing CO was cooled with liquid nitrogen to eliminate any contamination originating from metal carbonyls, while NO was cleaned with multiple freeze–pump–thaw cycles. Prior to spectrum collection, a background with the activated (annealed, reduced or oxidized) sample in the IR beam was collected. Each spectrum reported is obtained by averaging 64 scans.

HAADF-STEM was performed with a FEI Titan 80-300 microscope operated at 300 kV. The instrument is equipped with a CEOS GmbH double-hexapole aberration corrector for the probe-forming lens, which allows for imaging with 0.1 nm resolution in scanning transmission electron microscopy mode (STEM). The images were acquired with a high angle annular dark field (HAADF) detector with inner collection angle set to 52 mrad.

Computational Details and Models
Periodic DFT calculations were performed using the Perdew-Burke-Ernzerhof (PBE),[1] exchange-correlation functional with the additional empirical dispersion correction as proposed by Grimme (DFT-D2), [2] as implemented in Vienna ab initio simulation package (VASP). [3,4]. We also employed PAW pseudopotentials [5,6] and the valence wave functions were expanded in a
plane-wave basis with a cutoff energy of 415 eV. The Brillouin zone was sampled using only the \Gamma point.[7]

We used a monoclinic unit cell of the CHA framework, which consists of 36 T atoms. It was optimized for the pure silicate structure with dimensions: \(a = b = 13.675 \text{ Å}, c = 14.767 \text{ Å}; \alpha = \beta = 90^\circ, \gamma = 120^\circ\) [8]. One Si center in the unit cell located in one six-member ring was replaced with Al, as the negative charge around this Al was compensated by an H\(^+\) cation. During the geometry optimization, atoms were allowed to relax until the force on each atom became less than \(5 \times 10^{-2} \text{ eV/Å}\).

The vibrational frequencies were calculated using a normal mode analysis where the elements of the Hessian were approximated as finite differences of gradients, displacing each atomic center by \(1.5 \times 10^{-2} \text{ Å}\) either way along each Cartesian direction.

The reported binding energies (BE) of the various adsorbates (CO, CO\(_2\), NO, HNO\(_3\), HNO\(_2\)) were calculated as \(\text{BE} = - E_{\text{ad}} - E_{\text{sub}} + E_{\text{ad/sub}}\), where \(E_{\text{ad}}\) is the total energy of the adsorbate in the gas phase (ground state), \(E_{\text{sub}}\) is the total energy of the pristine zeolite system, where the framework negative charges are compensated by some of the modeled cationic species (H\(^+\), NO\(^+\), or NO\(_2^+\)) considered, and \(E_{\text{ad/sub}}\) is the total energy of the zeolite, together with the adsorbate in the optimized geometry. With the above definition, negative values of BE imply a favorable interaction.

When Gibbs free energies were obtained the enthalpy values were calculated from the total energy values (\(E_{\text{el}}\)) corrected for the internal vibrational energy (\(E_v\)) [9] and zero point vibrations (ZPE) derived from frequency calculations of the optimized structures: \(H_{140} = E_{\text{el}} + E_v + \text{ZPE}\).

The entropy values of the initial and transition states (TS) include only the vibrational degrees of freedom (\(S_v\)), since the adsorbates are bound to the zeolite and the rotational and translational degrees of freedom are converted into vibrations [10, 11]. The expressions of all enthalpy and entropy contributions can be found elsewhere [9].

References


Fig. S1. Difference spectra during \textit{in-situ} FTIR during sequential NO$_2$ adsorption (2 Torr) at room temperature on H-SSZ-13 with Si/Al ~ 6.
Fig. S2. Representative HAADF-STEM images of small-pore SSZ-13 crystals employed in this study.
Fig. S3. In-situ FTIR during heating of nitrosyl/SSZ-13 from 77 K (blue spectrum) to 298 K (red spectrum).
Fig. S4. In-situ FTIR during continuous heating of Nitrosyl/SSZ-13 at 200 °C under high vacuum (10⁻⁸ Torr) from time=0 (red spectrum) to time=1 hour (blue spectrum).
Fig. S5. FTIR during in-situ adsorption of excess NO₂ (2 Torr) on NO⁺/SSZ-13 system with Si/Al ~6 obtained through NO₂ disproportionation on H-SSZ-13 with Si/Al ~ 6.
Fig. S6. In-situ FTIR during NO (0.5 Torr) and O$_2$ (0.1 Torr) co-adsorption on H-SSZ-13 with Si/Al~12.
Fig. S7. In-situ FTIR during desorption of excess NO$_2$ (2 Torr) from NO$^+$-NO$_2$ system under continuous vacuum (10$^{-7}$ Torr) for 10 minutes for H-SSZ-13 with Si/Al ~ 12 (complementary to Fig. 1 C).
Fig. S8. In-situ FTIR during desorption of excess NO\textsubscript{2} (2 Torr) from NO\textsuperscript{+}-NO\textsubscript{2} system under continuous vacuum (10\textsuperscript{-7} Torr) for ~15 minutes for H-SSZ-13 with Si/Al ~ 6.
Fig. S9. In-situ FTIR during heating of NO⁺-CO/H-SSZ-13 system with Si/Al ~12
[NO⁺substoichiometric amount of O₂ were first reacted with zeolite to produce NO⁺ with only traces of nitrate, then vacuumed at 298 K, then cooled down to 100 K and reacted with 2 Torr CO at this temperature] during continuous heating from 100 K (red spectrum) to 270 K (red spectrum). No CO₂ evolution was observed above trace amounts.
Fig. S10.  
Structures of Zeo/NO<sup>+</sup>-NO<sub>2</sub> (left panel) and Zeo/NO<sup>+</sup>-NO (right panel) complexes. Color coding: Si – blue, O – red, Al – green, N – light blue, C – brown, H – white.

Fig. S11. Energy diagram of the mechanism of CO oxidation by NO<sub>2</sub><sup>+</sup>-CHA. The corresponding IS, TS, and FS structures are also shown. Color coding: Si – blue, O – red, Al – green, N – light blue, C – brown, H – white.
Table S1

Binding energy (in kJ/mol) of NO₂ and NO to Zeo/NO⁺ structure, vibrational frequencies (in cm⁻¹), ν(N-O), as well as selected interatomic distances, R(A-B), in pm.

<table>
<thead>
<tr>
<th>Structure</th>
<th>BE</th>
<th>ν(N-O)</th>
<th>R(N-N)</th>
<th>R(N-O)</th>
<th>R(O_{Zeo}-N(NO⁺))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO⁺ a</td>
<td>2404</td>
<td></td>
<td></td>
<td>109</td>
<td></td>
</tr>
<tr>
<td>NOF a</td>
<td>1920</td>
<td></td>
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<td>115</td>
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<td>ONNO a</td>
<td>1727, 1879</td>
<td>199</td>
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<td>Zeo/NO⁺-NO₂ -21</td>
<td>1722, 2042</td>
<td>272</td>
<td>113.1</td>
<td>214, 222</td>
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<td>Zeo/NO⁺-NO -52</td>
<td>2009, 1911</td>
<td>229</td>
<td>114.4, 114.6</td>
<td>223, 232</td>
<td></td>
</tr>
</tbody>
</table>

a gas phase species; b distances between zeolite O center and N atom from the charge-compensating NO⁺ species