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## Identification of the mechanism of NO reduction with ammonia (SCR) on zeolite catalysts†

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Cu/zeolites efficiently catalyze selective reduction of environmentally harmful nitric oxide with ammonia. Despite over a decade of research, the exact NO reduction steps remain unknown. Herein, using a combined spectroscopic, catalytic and DFT approach, we show that nitrosyl ions (NO<sup>+</sup>) in zeolitic micropores are the key intermediates for NO reduction. Remarkably, they react with ammonia even below room temperature producing molecular nitrogen (the reaction central to turning the NO pollutant to benign nitrogen) through the intermediacy of the diazo N<sub>2</sub>H<sup>+</sup> cation. Experiments with isotopically labeled N-compounds confirm our proposed reaction path. No copper is required for N<sub>2</sub> formation to occur during this step. However, at temperatures below 100 °C, when NO<sup>+</sup> reacts with NH<sub>3</sub>, the bare Brønsted acid site becomes occupied by NH<sub>3</sub> to form strongly bound NH<sub>4</sub><sup>+</sup>, and consequently, this stops the catalytic cycle, because NO<sup>+</sup> cannot form on NH<sub>4</sub>-zeolites when their H<sup>+</sup> sites are already occupied by NH<sub>4</sub><sup>+</sup>. On the other hand, we show that the reaction becomes catalytic on H-zeolites at temperatures when some ammonia desorption can occur (>120 °C). We suggest that the role of Cu(II) ions in Cu/zeolite catalysts for low-temperature NO reduction is to produce abundant NO<sup>+</sup> by the reaction: Cu(II) + NO → Cu(I)···NO<sup>+</sup>. NO<sup>+</sup> then reacts with ammonia to produce nitrogen and water. Furthermore, when Cu(I) gets re-oxidized, the catalytic cycle can then continue. Our findings provide novel understanding of the hitherto unknown steps of the SCR mechanism pertinent to N–N coupling. The observed chemistry of Cu ions in zeolites bears striking resemblance to the copper-containing denitrification and annamox enzymes, which catalyze transformation of NO<sub>x</sub> species to N<sub>2</sub>, *via* di-azo compounds.

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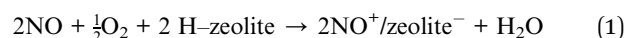
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Air pollution is one of the main health and environmental concerns in our (post)industrial society.<sup>1–3</sup> Worsened air quality during industrial expansion is attributed to a great extent to toxic nitric oxide (NO) gas, where nearly 55% of the global emissions are due to transportation exhaust. The ability of Cu/zeolites to turn NO to N<sub>2</sub> in the presence of ammonia was first discovered in Japan in the 1960s<sup>4</sup> for the Cu/FAU zeolite. However, the FAU framework is less stable than the corresponding SSZ-13 and BEA zeolites.<sup>5</sup> Within the last decade, the

ammonia selective catalytic reduction (SCR) technology was implemented on the large scale<sup>5–18</sup> for diesel engines on the basis of Cu(Fe) in BEA and SSZ-13 zeolites.

Some advances were achieved towards the goal of understanding the rate-limiting steps of the SCR mechanism.<sup>5–19</sup> Cu(II) ions are present in Cu/zeolite materials as well as Cu(II)–OH ions.<sup>5–19,24</sup> The rate-limiting step for low-temperature SCR, for low copper loaded materials (Cu loading below 0.5 wt%), was shown to be the re-oxidation of reduced Cu(I)(NH<sub>3</sub>)<sub>2</sub> complexes *via* the formation of transient (NH<sub>3</sub>)<sub>2</sub>Cu(II)–O<sub>2</sub>–Cu(II)(NH<sub>3</sub>)<sub>2</sub> dimers.<sup>16,17</sup> However, the steps involved in the exact mechanism of NO reduction to N<sub>2</sub> have remained unknown,<sup>5–19</sup> and the proposed DFT steps were shown hard to prove/observe experimentally.

In this study, we selectively formed NO<sup>+</sup> ions in H-BEA zeolite (typical helium ion microscopy images of H-BEA are shown in Fig. S0†) by the reaction of NO with O<sub>2</sub> (Fig. 1A).<sup>20–22</sup> NO<sup>+</sup> is formed through the reaction depicted in eqn (1):



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$\text{NO}^+$  occupies two different cationic positions with the corresponding N–O stretching frequencies at  $\sim 2133$  and  $\sim 2175 \text{ cm}^{-1}$ . The same type of chemistry also occurs on H-SSZ-13 (Fig. S1†). Note that adsorption of  $\text{NO}_2$  also produces  $\text{NO}^+$  but with stoichiometric  $\text{NO}_3^-$  amounts due to  $\text{N}_2\text{O}_4$  disproportionation (Fig. S2†). Our DFT calculations further corroborate the described chemistry *vide infra*.

Evacuation to high vacuum ( $\sim 10^{-7}$  Torr) (with quick heating to  $150^\circ\text{C}$ ) allows the removal of excessive  $\text{NO}$  and  $\text{O}_2$ , leaving the zeolite with  $\text{NO}^+$  adsorbed in it (Fig. 1B).

We exposed the  $\text{NO}^+$ /zeolite to  $^{15}\text{N}$ -labeled ammonia at room temperature ( $\sim 20^\circ\text{C}$ ) (Fig. 2A). Ammonia first occupies Brønsted acid sites forming  $\text{NH}_4^+$  complexes which interact with  $\text{NH}_3$  in the pores, generating  $(\text{NH}_3)_x$  cluster networks interacting with  $\text{NH}_4^+$  ions.<sup>23,26</sup> During this,  $\text{NO}^+$  reacts with ammonia, as evidenced by the swiftly diminishing  $\text{NO}^+$  band,

eventually leaving no new visible  $\text{NO}$  stretches as the excess of  $^{15}\text{NH}_3$  produces the complex bands typical for  $\text{NH}_4^+(\text{NH}_3)_x$  clusters in zeolites in the  $2250\text{--}1750 \text{ cm}^{-1}$  region<sup>24</sup> (Fig. 2A).

The analysis of the gas-phase product by mass-spectrometry reveals a major peak at 29 amu per charge, corresponding to  $^{14}\text{N}\text{--}^{15}\text{N}$  molecules (Fig. 2B). Thus,  $\text{NO}^+$  reacts with ammonia to form molecular nitrogen at room temperature on H-BEA. Eqn (2) and (3) can be used to describe this process. Note that  $\text{NO}^+$  does not necessarily have to be bound to zeolite in the presence of  $\text{NH}_3$  and can initially become solvated by  $\text{NH}_3$  (it is well-known that ammonia has propensity to solvate cationic species in and outside zeolites;<sup>16,17,24</sup> our DFT calculations in Table 1 further confirm strong favorability of  $\text{NO}^+$  solvation by ammonia with an energy gain of  $95 \text{ kJ mol}^{-1}$ ); the designation zeolite- $\text{NO}^+$  is just a representation of the  $\text{NO}^+$ /H-zeolite system

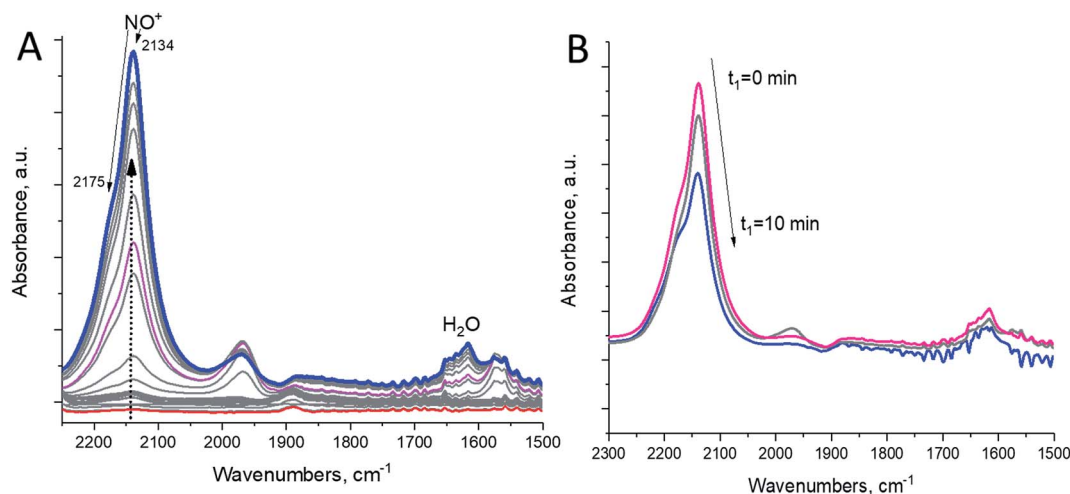


Fig. 1 H-BEA zeolite with Si/Al  $\sim 15$ . (A, left spectrum) *In situ* FTIR during the first sequential  $\text{NO}$  adsorption (0.1 Torr equilibrium pressure), followed by sequential  $\text{O}_2$  addition (0.17 Torr total eq. pressure – when  $\text{O}_2$  is added,  $\text{NO}^+$  begins to develop in significant amounts);  $T = 20^\circ\text{C}$ . (B, right spectrum) FTIR spectra collected after pulling high vacuum  $10^{-8}$  Torr from time = 0 to time = 10 minutes at  $150^\circ\text{C}$ . Spectra were recorded after cooling back to  $20^\circ\text{C}$ .

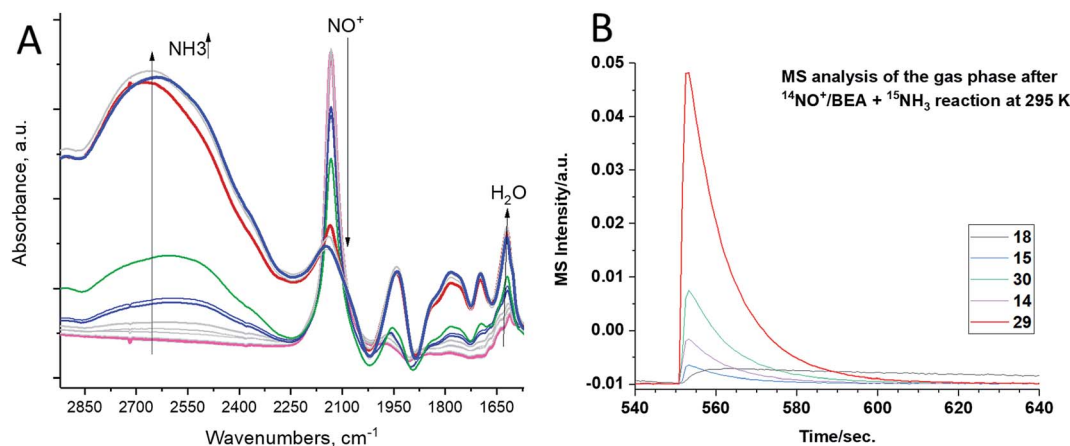


Fig. 2 H-BEA zeolite with Si/Al  $\sim 15$ . (A, left spectrum) *In situ* sequential FTIR during  $^{15}\text{NH}_3$  adsorption (total equilibrium pressure 0.020 Torr) on the  $\text{NO}^+$ /H-BEA sample at  $20^\circ\text{C}$ . Ammonia reacts with  $\text{NO}^+$ . The gas phase effluent from the reaction ( $T = 20^\circ\text{C}$ ) was analyzed with a mass spectrometer attached to an IR cell. (B) shows formation of  $^{14}\text{N}\text{--}^{15}\text{N}$  dinitrogen with the characteristic  $m/z = 29$  signal.

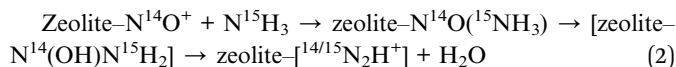


Table 1 Energies,  $\Delta E$ , and activation barriers,  $E_a$ , of the modelled reaction steps

Reaction	$\Delta E$ , kJ mol <sup>-1</sup>	$E_a$ , kJ mol <sup>-1</sup>
<b>Direct participation of the chabazite</b>		
$\text{NO}^+/\text{Zeolite} + \text{NH}_3(\text{g}) \rightarrow \text{NO}^+(\text{NH}_3)/\text{Zeolite}$	-97	—
$\text{NO}^+(\text{NH}_3)/\text{Zeolite} \rightarrow \text{NONH}_2/\text{H}^+-\text{Zeolite}$	-7	5
$\text{NONH}_2/\text{H}^+-\text{Zeolite} \rightarrow \text{NONH}_2\text{-rotated1}/\text{H}^+-\text{Zeolite}$	-31	—
$\text{NONH}_2\text{-rotated1}/\text{H}^+-\text{Zeolite} \rightarrow \text{HN}=\text{NOH}/\text{H}^+-\text{Zeolite}$	12	13
$\text{HN}=\text{NOH}/\text{H}^+-\text{Zeolite} \rightarrow \text{HN}=\text{NOH\_rotated1}/\text{H}^+-\text{Zeolite}$	18	—
$\text{HN}=\text{NOH\_rotated1} \rightarrow (\text{N}_2 + \text{H}_2\text{O})/\text{H}^+-\text{Zeolite}$	-225	8
$\text{HN}=\text{NOH}/\text{H}^+-\text{Zeolite} \rightarrow \text{HN}=\text{NOH\_rotated2}/\text{H}^+-\text{Zeolite}^a$	29	—
$\text{HN}=\text{NOH\_rotated2}/\text{H}^+-\text{Zeolite} \rightarrow (\text{NNH}^+ + \text{H}_2\text{O})/\text{Zeolite}^a$	-8	14
$(\text{NNH}^+ + \text{H}_2\text{O})/\text{Zeolite} \rightarrow (\text{NNH}^+\text{-rotated} + \text{H}_2\text{O})/\text{Zeolite}^a$	-21	—
$(\text{NNH}^+\text{-rotated} + \text{H}_2\text{O})/\text{Zeolite} \rightarrow (\text{N}_2 + \text{H}_2\text{O})/\text{H}^+-\text{Zeolite}^a$	-207	2
<b>No direct participation of the chabazite at some reaction steps</b>		
$\text{NO}^+/\text{Zeolite} + \text{NH}_3 \rightarrow \text{NO}^+(\text{NH}_3)/\text{Zeolite}$	-95	—
$\text{NO}^+(\text{NH}_3)/\text{Zeolite} \rightarrow \text{NONH}_2\text{-rotated3}/\text{H}^+-\text{Zeolite}$	-40	131
$\text{NONH}_2\text{-rotated3}/\text{H}^+-\text{Zeolite} \rightarrow \text{HN}=\text{NOH\_rotated3}/\text{H}^+-\text{Zeolite}$	41	148
$\text{HNNOH\_rotated3}/\text{H}^+-\text{Zeolite} \rightarrow (\text{N}_2 + \text{H}_2\text{O})/\text{H}^+-\text{Zeolite}$	-236	—
<b>PhNH<sub>2</sub> transformation in the pores of Zeolite/NO<sup>+</sup></b>		
$\text{NO}^+/\text{Zeolite} + \text{PhNH}_2(\text{g}) \rightarrow (\text{PhNH}_2\text{-NO}^+)/\text{Zeolite}$	-186	—
$(\text{PhNH}_2\text{-NO}^+)/\text{Zeolite} \rightarrow \text{PhNH}=\text{NO}/\text{H}^+-\text{Zeolite}$	5	31
$\text{PhNH}=\text{NO}/\text{H}^+-\text{Zeolite} \rightarrow \text{PhNH}=\text{NOH}^+/\text{Zeolite}$	-49	3
$\text{PhNH}=\text{NOH}^+/\text{Zeolite} \rightarrow \text{PhN}=\text{NOH}/\text{H}^+-\text{Zeolite}$	57	65
$\text{PhN}=\text{NOH}/\text{H}^+-\text{Zeolite} \rightarrow (\text{PhN}=\text{N}^+ + \text{H}_2\text{O})/\text{Zeolite}$	-69	11
$(\text{PhN}=\text{N}^+ + \text{H}_2\text{O})/\text{Zeolite} \rightarrow \text{PhN}=\text{N}^+/\text{Zeolite} + \text{H}_2\text{O}(\text{g})$	26	—
$\text{PhNH}=\text{NOH}^+/\text{Zeolite} \rightarrow (\text{PhN}=\text{N}^+ + \text{H}_2\text{O})/\text{Zeolite}^b$	-12	158
$\text{PhNH}=\text{NO}/\text{H}^+-\text{Zeolite} \rightarrow \text{PhN}=\text{NOH\_rotated}/\text{H}^+-\text{Zeolite}^c$	-4	1
$\text{PhN}=\text{NOH\_rotated}/\text{H}^+-\text{Zeolite} \rightarrow (\text{PhN}=\text{N}^+ + \text{H}_2\text{O})/\text{Zeolite}^c$	-57	23
<b>Interaction of BF<sub>4</sub>/NO<sup>+</sup> with NH<sub>3</sub></b>		
$\text{NO}^+/\text{BF}_4^- + \text{NH}_3(\text{g}) \rightarrow \text{NO}^+(\text{NH}_3)/\text{BF}_4^-$	-91	—
$\text{NO}^+(\text{NH}_3)/\text{BF}_4^- \rightarrow \text{NONH}_2/\text{BF}_3\text{-HF}$	15	16
$\text{NONH}_2/\text{BF}_3\text{-HF} \rightarrow \text{NONH}_2\text{-rotated1}/\text{BF}_3\text{-HF}$	-42	—
$\text{NONH}_2\text{-rotated1}/\text{BF}_3\text{-HF} \rightarrow \text{HN}=\text{NOH}/\text{BF}_3\text{-HF}$	-3	2
$\text{HN}=\text{NOH}/\text{BF}_3\text{-HF} \rightarrow \text{HN}=\text{NOH\_rotated1}/\text{BF}_3\text{-HF}$	31	—
$\text{HN}=\text{NOH}/\text{BF}_3\text{-HF\_rotated1} \rightarrow (\text{N}_2 + \text{H}_2\text{O})/\text{BF}_3\text{-HF}$	-221	1
$\text{HN}=\text{NOH}/\text{BF}_3\text{-HF} \rightarrow \text{HN}=\text{NOH\_rotated2}/\text{BF}_3\text{-HF}^d$	44	—
$\text{HN}=\text{NOH\_rotated2}/\text{BF}_3\text{-HF} \rightarrow (\text{NNH}^+ + \text{H}_2\text{O})/\text{BF}_4^-^d$	-17	16
$\text{NONH}_2/\text{BF}_3\text{-HF} \rightarrow \text{NONH}_2\text{-rotated2}/\text{BF}_3\text{-HF}^e$	-25	—
$\text{NONH}_2\text{-rotated2}/\text{BF}_3\text{-HF} \rightarrow \text{HN}=\text{NOH\_rotated3}/\text{BF}_3\text{-HF}^e$	17	126

<sup>a</sup> Alternative reaction paths: marked in red color in Fig. 7B. <sup>b</sup> Marked in red color in Fig. 9. <sup>c</sup> Marked in blue color in Fig. 9. <sup>d</sup> Marked in red color in Fig. 10. <sup>e</sup> Marked in blue color in Fig. 10.

in which  $\text{NO}^+$  may be solvated or semi-solvated by ammonia molecules.



The hydronium diazonium cation ( $\text{N}_2\text{H}^+$ ) is extremely unstable. Its immediate decomposition to  $\text{N}_2$  and H-zeolite drives the reaction forward. Despite this, we find that at sufficiently high molecular  $\text{N}_2$  pressure in the cell ( $\sim 15$  Torr), we can observe a small N-N stretch of the  $\text{-HN}_2^+$  complex at  $2334\text{ cm}^{-1}$  even at room temperature (Fig. 3A), which was previously shown

to form at low temperatures upon  $\text{N}_2$  interaction with Brønsted acid sites (Fig. 3B).<sup>25-27</sup>

To provide proof that the reaction proceeds through a diazo compound, we chose aniline  $\text{PhNH}_2$ , an equivalent of the ammonia molecule but with 1 hydrogen atom substituted by a phenyl group, and it reacted with  $\text{NO}^+$  in the BEA zeolite. The phenyl group stabilizes the formation of  $\text{PhN}_2^+$  salts (phenyl diazonium salts) through the mesomeric effect, and unlike alkyl diazonium salts, aryl diazonium compounds are stable and characterized by N-N stretches in the  $\sim 2250\text{--}2300\text{ cm}^{-1}$  region, more specifically  $\sim 2270\text{ cm}^{-1}$  for phenyl diazonium in solution.<sup>28</sup> Indeed, we monitored the reaction of  $\text{NO}^+$  and  $\text{PhNH}_2$ , spectroscopically: the intensity of the  $\text{NO}^+$  band diminished, and a new N-N stretch appeared at  $\sim 2270\text{ cm}^{-1}$ , corresponding to the N-N vibration of the  $\text{Ph-N}_2^+$  fragment (Fig. 4). The reaction of  $\text{NO}^+$  with  $\text{NH}_3$  is more sluggish than with  $\text{NH}_3$ ,



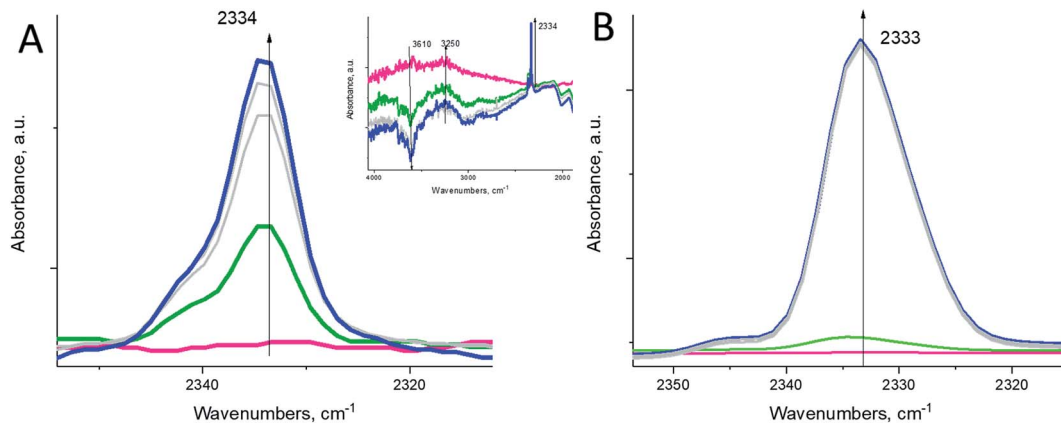


Fig. 3 (A, left spectrum) *In situ* FTIR during sequential dinitrogen  $N_2$  adsorption (equilibrium pressure  $\sim 15$  Torr) on H-BEA at  $\sim 23$  °C. A very unstable zeolite- $[HN_2]^+$  complex can be observed even at room temperature, but it requires elevated  $N_2$  pressure. The inset shows that  $N_2$  interacts with Brønsted acid sites of Si-OH-Al zeolite groups (OH stretch of such groups is located at  $\sim 3610$   $cm^{-1}$ ). (B, right spectrum) *In situ* FTIR during adsorption of only  $\sim 0.1$  Torr  $N_2$  on the same H-BEA sample (equilibrium pressure is 0.001 Torr) at 77 K produces N-N stretches of  $N_2$  adsorbed on Brønsted acid sites. Note that in this case, even low equilibrium pressure of nitrogen produces intense N-N stretches.

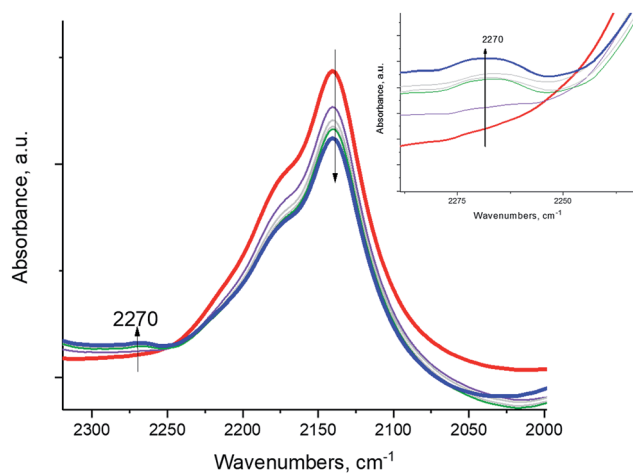
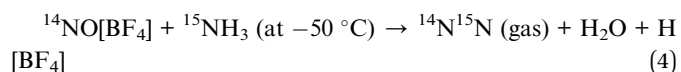


Fig. 4 *In situ* FTIR during sequential  $\sim 0.3$  Torr aniline  $PhNH_2$  adsorption (equilibrium pressure  $\sim 0.03$  Torr)  $NO^+/H$ -BEA.

consistent with the higher activation barrier calculated for  $PhN_2^+$  formation (Table 1). This is the first observation of a diazo-salt stabilized on a solid support (zeolite).

$NO^+$  in H-SSZ-13 (with Si/Al  $\sim 12$ ; typical HAADF-STEM images of this sample are shown in Fig. S7†) reacts similarly with  $NH_3$  (Fig. 5), with concomitant  $N_2$  evolution (confirmed by mass spectrometry):

As such,  $NO^+$  is the critical intermediate species in the conversion of NO in these zeolites. Copper is not required to observe the  $NO^+$  reactivity with  $NH_3$ . Moreover, we reacted inorganic nitrosyl salt  $NO^+$  with  $^{15}NH_3$  and observed  $^{14}N$ - $^{15}N$  in the gas-phase (consistent with our findings for  $NO^+$  in zeolites; this reaction takes place vigorously even at a temperature as low  $-50$  °C) (eqn (4)):



This reaction (eqn (4)) most likely proceeds through the  $N_2H^+$  intermediate as well.

For  $NO^+$  in the zeolite, once it reacts with  $NH_3$  with the release of  $N_2$ , the Brønsted acid is free and immediately interacts with ammonia to produce  $NH_4^+$ . This latter process “kills” the reactivity as the  $NO^+$  species can no longer be produced due to the necessity of Brønsted acid sites, as evidenced by FTIR (Fig. S4†); indeed, no  $NO^+$  evolves above trace amounts upon the  $NO + O_2$  reaction on the  $NH_4$ -zeolite (Fig. S4†). Only at elevated temperatures, when some  $NH_3$  can desorb and free up a portion of Brønsted acid sites to re-form  $NO^+$ , can the reaction proceed

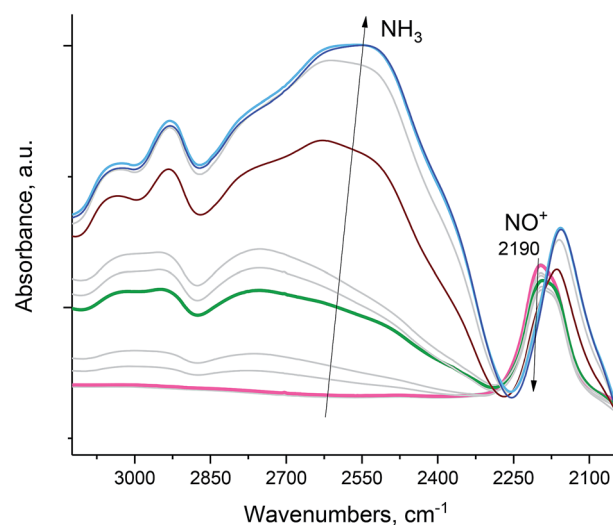


Fig. 5 H-SSZ-13 zeolite with Si/Al  $\sim 12$ . *In situ* sequential FTIR during  $^{14}NH_3$  adsorption (total equilibrium pressure  $\sim 0.15$  Torr) on the  $NO^+/H$ -SSZ-13 sample at 20 °C. Ammonia reacts with  $NO^+$  as evidenced by the disappearance of the  $NO^+$  stretch. The intense band at  $\sim 2110$   $cm^{-1}$  is due to zeolite interactions with  $NH_3$ . Pulling vacuum on the sample at 120 °C produces spectra showing no  $NO^+$  stretches (Fig. S3†), consistent with the complete reaction of  $NO^+$ .



catalytically which we show in Fig. S5.† The bare H-BEA zeolite is catalytically active for NO reduction with NH<sub>3</sub> in dry streams (see Fig. S5† for reactivity at 200 and 150 °C with time-on-stream) (measurable activity is observed). NO<sup>+</sup> is formed in zeolite through eqn (1) (see the earlier discussion in the manuscript).

With these new data, we can now further explain the possible role of Cu in zeolites for SCR. As is well-established in the literature, Cu(II) ions are required for the continuous catalytic reaction to proceed.<sup>5–19</sup> In the presence of NO, Cu(II) ions can produce NO<sup>+</sup> *via* 1-electron reduction of Cu(II) (analogous chemistry is observed, for example, for Pd(II) in zeolites<sup>30</sup> where Pd(II) was shown to reduce to Pd(I) by NO pulses with the concomitant formation of NO<sup>+</sup>) (eqn (5)):



Fig. 6A shows spectroscopic evidence of Cu(II) reduction by NO (when Cu(II) is first reduced to Cu(I) prior to NO adsorption, very little NO<sup>+</sup> formation occurs because electron transfer does not take place in the absence of Cu(II) as demonstrated in Fig. 6B).

We have previously been able to confirm by solid-state <sup>15</sup>N NMR studies that NO indeed is capable of reducing Cu(II) to Cu(I) in SSZ-13: the resulting complex had Cu(I) and NO<sup>+</sup> in proximity to each other, with NO<sup>+</sup> located side-on towards a copper ion.<sup>19</sup> Similar chemistry is observed for Pd(II) in zeolites.<sup>29</sup>

The mechanism of NO<sup>+</sup>-zeolite formation from the H<sup>+</sup>-zeolite and NO and/or NO<sub>2</sub> has been investigated experimentally<sup>22,34</sup> and theoretically.<sup>35</sup> It was shown<sup>35</sup> that the barrier for NO<sup>+</sup> formation on H<sup>+</sup>-CHA from NO<sub>2</sub> is only 15 kJ mol<sup>-1</sup>, while the process is endothermic by only 2 kJ mol<sup>-1</sup>. Our novel experimental findings for NO<sup>+</sup> in zeolites prompted us to investigate the proposed reaction steps with density functional theory (DFT) calculations. First, we investigated two pathways

for selective catalytic reduction of NO by the ammonia *via* formation of the NO<sup>+</sup> species in the zeolite: (1) with the direct (Fig. 7, Table 1) participation of the zeolite and (2) without (Fig. 8, Table 1) the direct zeolite participation at some reaction steps. Both pathways start with adsorption of NH<sub>3</sub> to NO<sup>+</sup>/Zeo with a binding energy of ammonia of ~97 kJ mol<sup>-1</sup> and subsequent formation of nitrosamine *via* transfer of one of the H atoms from the ammonia to an O center from the AlO<sub>4</sub> tetrahedron.

When the reaction step occurs *via* direct H transfer, the energy barrier is only 5 kJ mol<sup>-1</sup> (Fig. 7B, Table 1). We also found another transition state (TS) structure with elongated N–H distance (Fig. 8, Table 1), and it is less stable by more than 120 kJ mol<sup>-1</sup> than the previous one, despite the fact that the zeolite participates in the reaction step since one of the H atoms from NH<sub>3</sub> is transferred to the zeolite as a proton. Further, one of the H atoms of the NH<sub>2</sub> group of the nitrosamine should migrate to the O center of the same molecule thus forming a HON=NH molecule. This can be done *via* H transfer occurring in the gas phase without the participation of the zeolite. In this case however, the reaction step is endothermic by 41 kJ mol<sup>-1</sup>, while the barrier is as high as 148 kJ mol<sup>-1</sup>. Alternatively, the process can occur stepwise with the direct participation of the zeolite support. In this case initially the molecule of nitrosamine reorients so that two hydrogen bonds are formed between the guest molecule and support: the N–H fragment with the O center from a zeolite and a zeolite proton with the O center from the nitrosamine. The new configuration is more stable by 31 kJ mol<sup>-1</sup> than the previous one.

Further, *via* a synchronous transition state structure, the H atom from the NH fragment moves to the zeolite O center, and simultaneously, the zeolite proton migrates to the O atom from the guest molecule. The energy barrier is only 13 kJ mol<sup>-1</sup>, while the reaction step is only slightly endothermic by 12 kJ mol<sup>-1</sup>. Similar energetics were also reported previously.<sup>36</sup> In the next

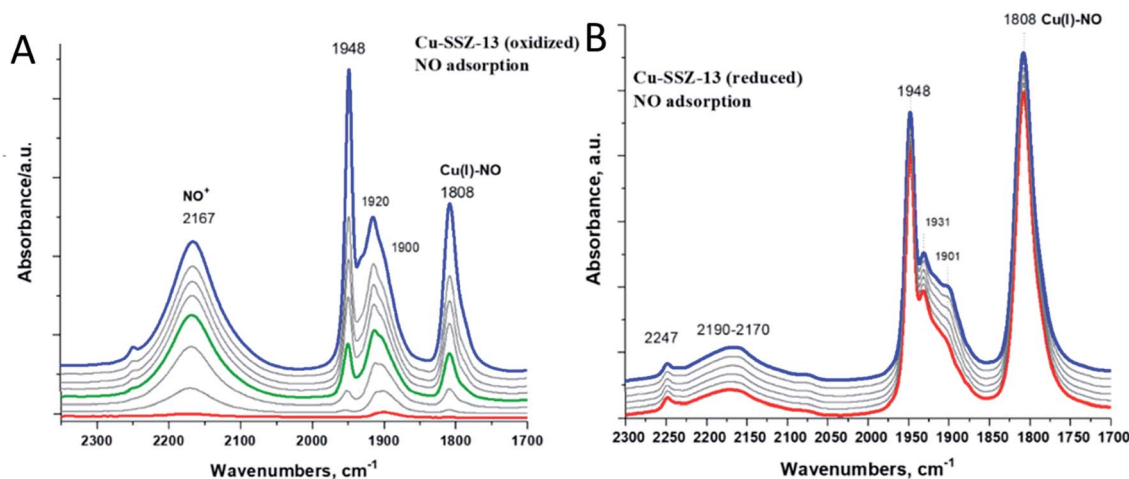


Fig. 6 1 wt% Cu/H-SSZ-13 sample with Si/Al ~ 12. (A) *In situ* FTIR during 1 Torr NO adsorption on the pre-oxidized sample (pre-oxidized in O<sub>2</sub> at 300 °C). NO<sup>+</sup> and Cu(I)–NO evolve simultaneously from Cu(II) reduction by NO. (B) The same sample (tablet) was pre-reduced in the IR cell (at 300 °C); 1 Torr NO adsorption (same equilibrium pressure) after reduction.



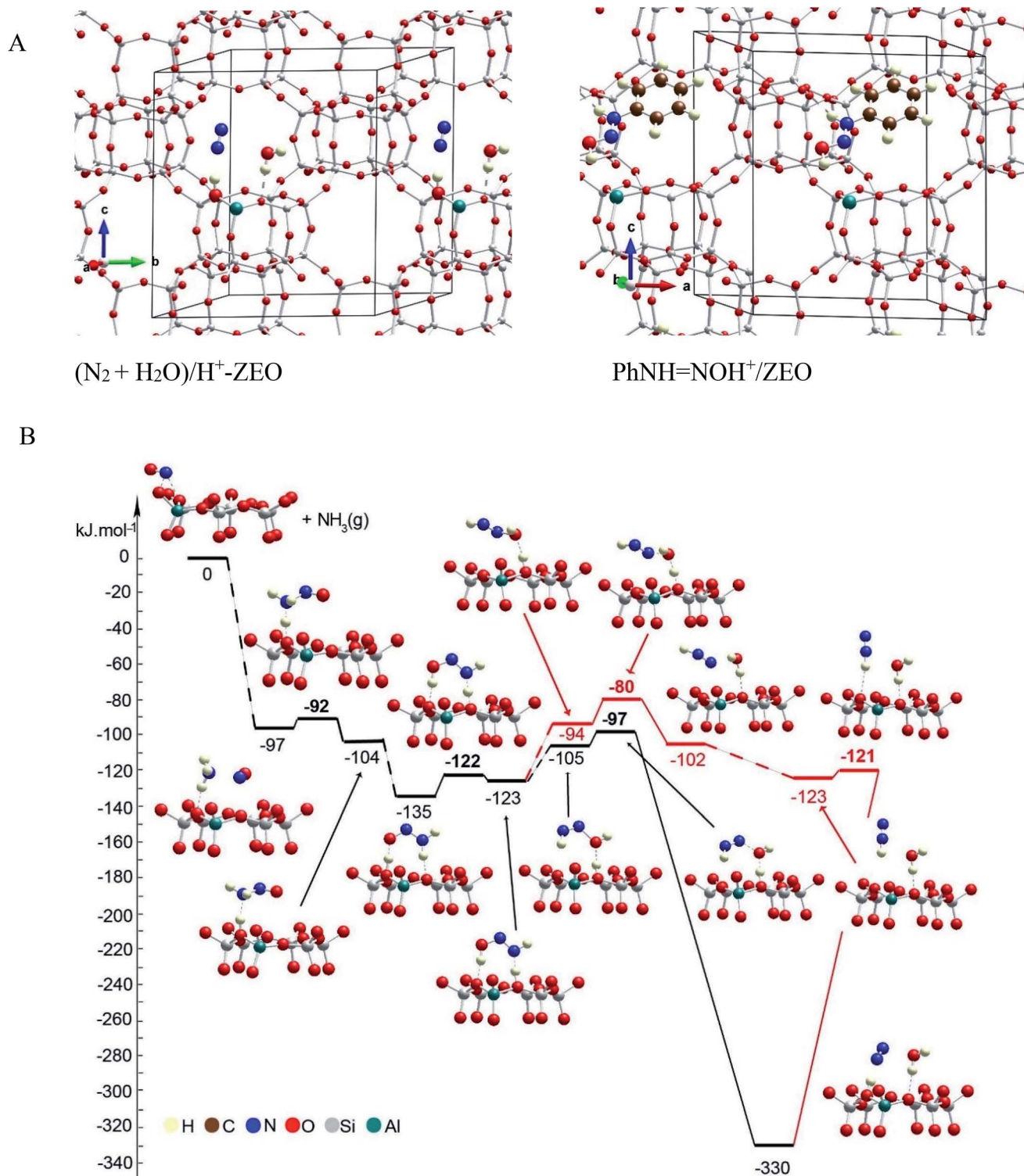


Fig. 7 (A) General location of the species in the pores of the unit cell of chabazite. Color coding: H – yellow; N – blue; C – brown; O – red; Al – green; Si – gray. (B) Energy diagram and optimized models of reaction steps with the direct participation of the chabazite. Alternative reaction paths are shown in different colors. The models are visualized with the VESTA program.<sup>33</sup>

step, the HON=NH molecule should be converted into the final products: H<sub>2</sub>O and N<sub>2</sub>. This can be done again *via* direct H transfer in the gas phase from the N to the O atom with no direct participation of the zeolite support. Based on the previous

knowledge, it is expected that the reaction step will have a high barrier. Alternatively, we considered the process with the participation of the zeolite, as two reaction pathways were considered: concerted and stepwise pathways, as in both cases,



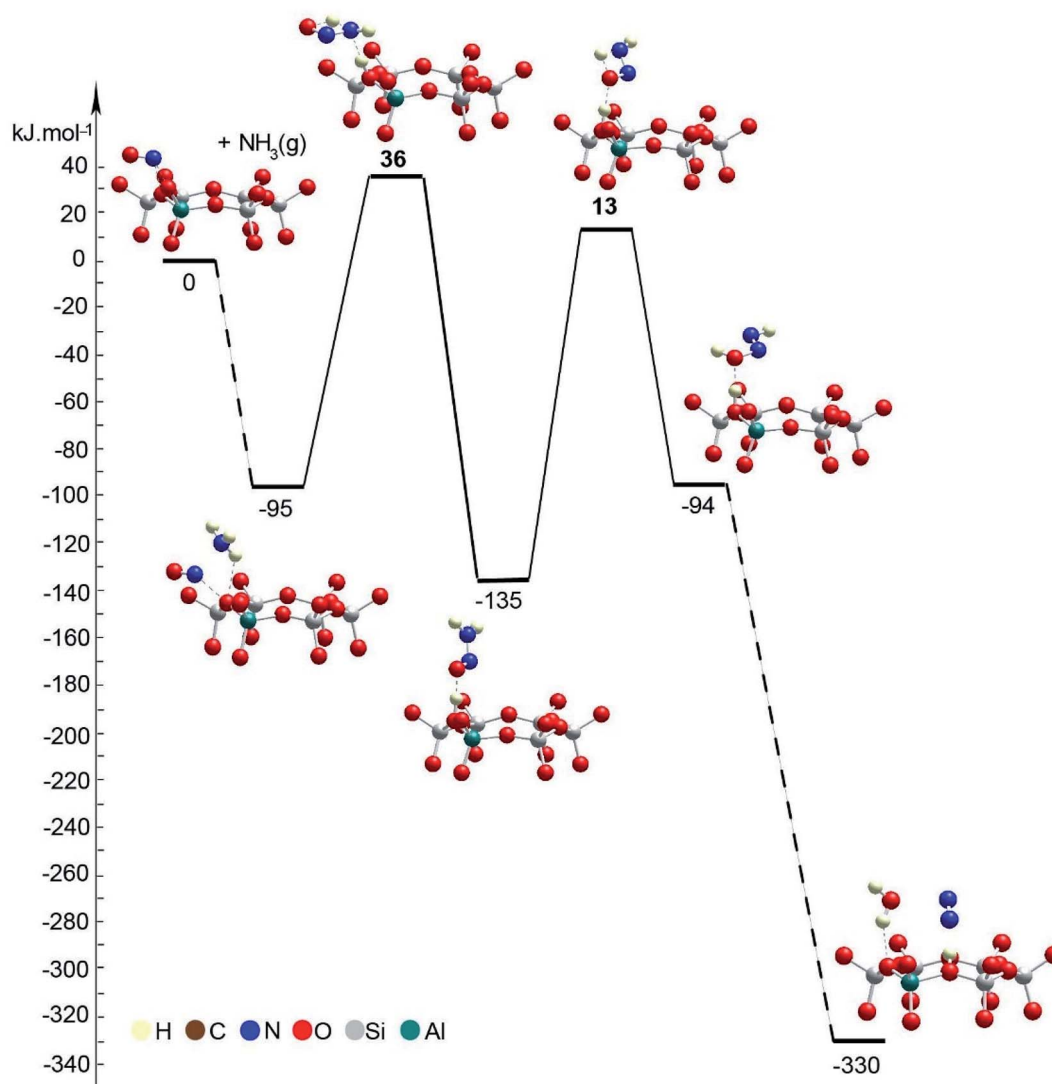


Fig. 8 Energy diagram and optimized models of reaction steps with no direct participation of the chabazite at some reaction steps. The models are visualized with the VESTA program.<sup>33</sup>

initially, the guest molecule changes its position with respect to the zeolite support as one of the hydrogen bonds,  $\text{NH}\cdots\text{O}$ , breaks. The new structures are less stable by 18 and 29  $\text{kJ mol}^{-1}$  than the final state structure of the previous reaction step. In the concerted mechanism, in one step, the zeolite proton moves to the OH group from the  $\text{HON}=\text{NH}$  species, thus forming a water molecule, while the H bound to the N atom moves to an O zeolite center forming a  $\text{N}_2$  molecule. The reaction step is strongly exothermic,  $-225 \text{ kJ mol}^{-1}$ , with a very low barrier, 8  $\text{kJ mol}^{-1}$ . The high exothermicity<sup>36,37</sup> and the low barrier<sup>36</sup> were also inferred in previous theoretical studies. Alternatively, in the stepwise mechanism,  $\text{H}_2\text{O}$  and  $\text{NNH}^+$  can be formed first, overcoming a low barrier of 14  $\text{kJ mol}^{-1}$  as the reaction step is slightly exothermic,  $-8 \text{ kJ mol}^{-1}$ . Next,  $\text{NNH}^+$  reorients so that a hydrogen bond is formed with the zeolite O center. In the final step, H moves to the zeolite O center; this bridging OH group and  $\text{N}_2$  molecule are formed. This step is essentially barrierless and strongly exothermic,  $-207 \text{ kJ mol}^{-1}$ . These DFT results

confirm favorability of  $\text{NO}^+$  interaction with  $\text{NH}_3$  to form  $\text{N}_2$  basically with little to no barriers, consistent with the experimentally observed low-temperature reactivity of these species. Similar mechanisms of  $\text{NH}_2\text{NO}$  decomposition were reported<sup>36,37</sup> as they considered additional steps of transfer of the zeolite proton from one basic O center to another assisted by the O or N atom in the  $\text{HNNOH}$ , which seems to be the highest ones according to the latter study. According to us, such steps can be omitted as shown by the mechanism proposed by us.

Next, we modeled the reduction process using aniline  $\text{PhNH}_2$  interacting with the  $\text{NO}^+$  species positioned as a charge-compensating cation in chabazite (Fig. 9, Table 1).

The adsorption energy of aniline to  $\text{NO}^+$  species is  $-186 \text{ kJ mol}^{-1}$ . Further, one of the H atoms of the amino groups migrates to the O center from the zeolite, thus forming  $\text{ONNHPh}$  coordinated to the zeolite proton. This reaction step is slightly endothermic by 5  $\text{kJ mol}^{-1}$ , and its energy barrier is



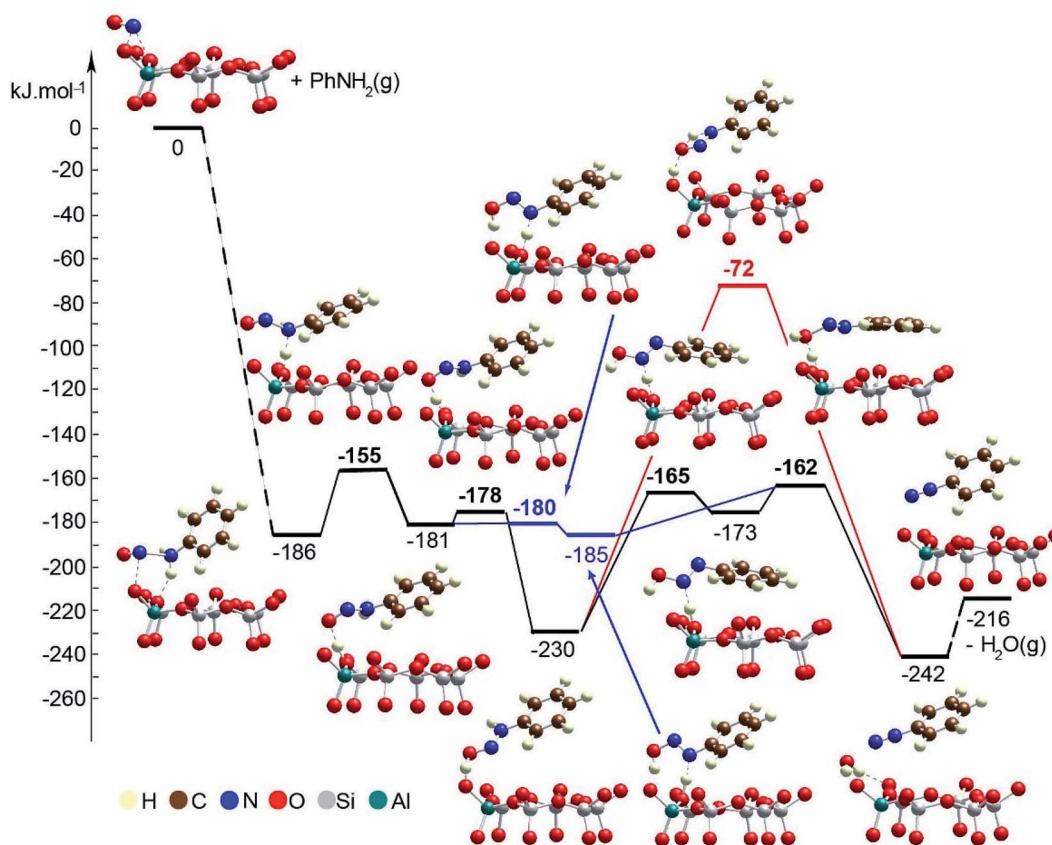


Fig. 9 Energy diagram and optimized models of the reaction steps for the  $\text{PhNH}_2$  transformation in the pores of  $\text{Zeo/NO}^+$ . The models are visualized with the VESTA program.<sup>33</sup>

$31 \text{ kJ mol}^{-1}$ . From the latter structure, one can obtain a benzenediazonium cation,  $\text{PhNN}^+$ , via two alternative pathways:

– In the more plausible pathway, the  $\text{HONNPh}$  structure is formed via a synchronous TS structure in which a zeolite proton migrates onto the O atom from the organic molecule, while the H atom from the NH fragment moves to a zeolite O center. The reaction step is essentially barrierless and very slightly exothermic,  $-4 \text{ kJ mol}^{-1}$ . Further, the zeolite proton interacts with the OH group from the organic molecule which leads to formation of  $\text{PhNN}^+$  and a water molecule. The barrier for this reaction step is  $23 \text{ kJ mol}^{-1}$ , and it is exothermic by  $57 \text{ kJ mol}^{-1}$ .

– The alternative pathway requires overcoming of higher barriers than in the first one. In the first step, the zeolite proton migrates to the O center from the organic molecule as  $\text{PhNH=NOH}^+$  is formed. The process is essentially barrierless and exothermic by  $49 \text{ kJ mol}^{-1}$ . At the final stage, a  $\text{PhNN}^+$  cation should be formed, as we considered two possible reaction pathways. In the concerted mechanism, in one step, the O center forms bonds with both H centers which are initially positioned at the zeolite O center and the N atom from the organic molecule. The second H transfer is in the gas phase without direct participation of the zeolite which leads to an unstable transition state structure, and thus, the barrier is  $158 \text{ kJ mol}^{-1}$ , and reaction energy is only slightly exothermic by  $12 \text{ kJ mol}^{-1}$ . In the stepwise mechanism, a H atom bound to the N center is

transferred to an O zeolite center forming a  $\text{HON=NPh}$  molecule. This reaction step is endothermic by  $57 \text{ kJ mol}^{-1}$ , and the barrier is  $65 \text{ kJ mol}^{-1}$ . Finally, the zeolite proton interacts with the OH group which leads to formation of  $\text{H}_2\text{O}$  and a  $\text{PhNN}^+$  cation. This step requires overcoming of a very low barrier,  $11 \text{ kJ mol}^{-1}$ , and it is exothermic by  $69 \text{ kJ mol}^{-1}$ .

Furthermore, because we observed that the  $\text{NO}^+$  reaction with ammonia is not exclusive to zeolite and that inorganic nitrosyl salts (such as  $\text{NO}[\text{BF}_4]$ ) react with ammonia to form molecular nitrogen at a temperature as low as  $-50 \text{ }^\circ\text{C}$ , two pathways for the SCR reaction with ammonia on  $\text{BF}_4^-/\text{NO}^+$  were investigated: (1) with and (2) without the direct participation of the boron fluoride complex (Fig. 10, Table 1). Both schemes start with adsorption of ammonia onto the  $\text{BF}_4^-/\text{NO}^+$  substrate forming the  $\text{H}_3\text{NNO}^+$  species, as the binding energy is  $-91 \text{ kJ mol}^{-1}$ . In the first step, one of the H atoms of  $\text{H}_3\text{NNO}^+$  moves to the  $\text{BF}_4^-$  anion. The reaction step is slightly endothermic by  $15 \text{ kJ mol}^{-1}$  and requires overcoming a barrier of  $16 \text{ kJ mol}^{-1}$ . In the final structure, the nitrosamine and hydrogen fluoride are produced and bound by a hydrogen bond between H from the  $\text{BF}_3\text{-HF}$  complex and the N from the amino group. Further, a rearrangement of the complex occurs, so that the O atom interacts with the proton from the  $\text{BF}_3\text{-HF}$  complex. This complex is more stable by  $25 \text{ kJ mol}^{-1}$  than the previous one, while if a second hydrogen bond is formed, a further





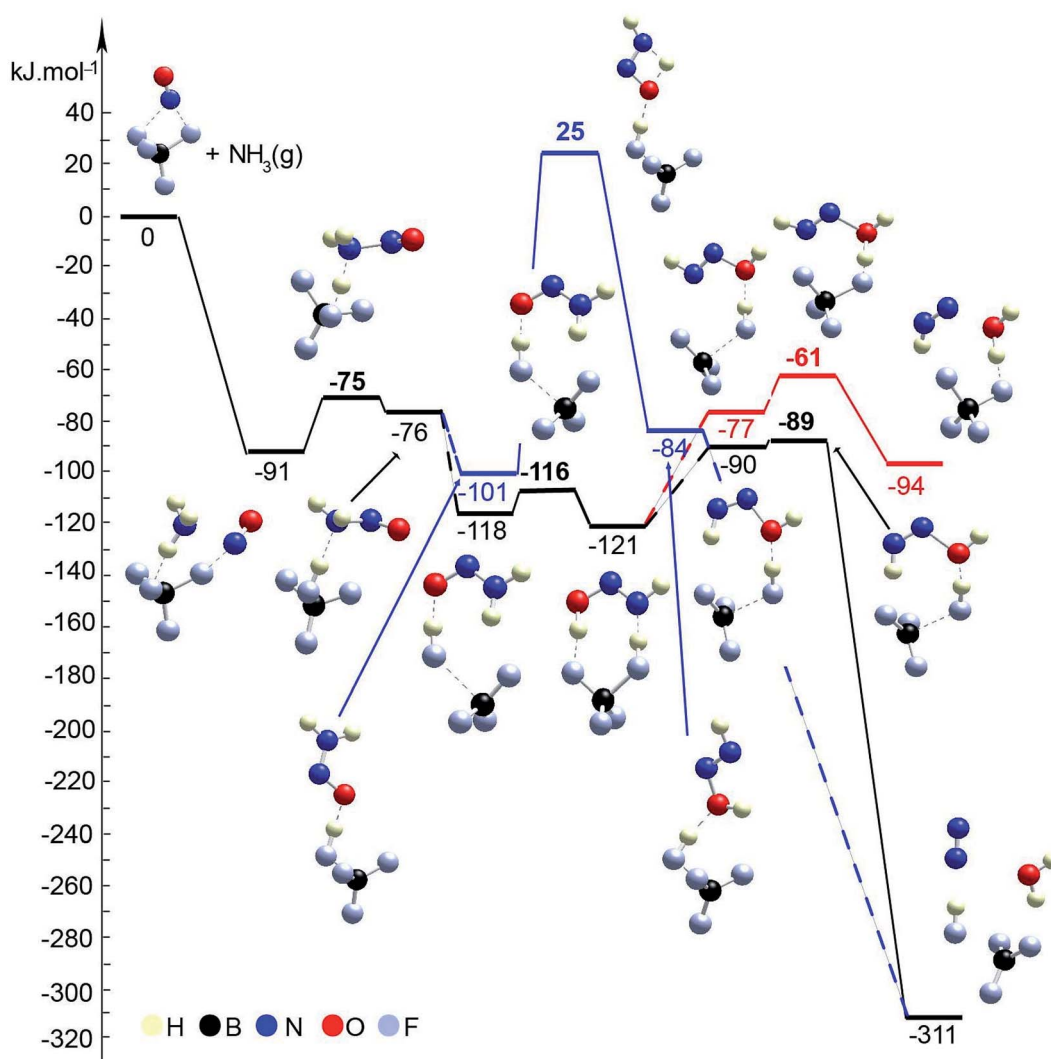


Fig. 10 Energy diagram and optimized models of reaction steps for the interaction of  $\text{BF}_4^-/\text{NO}^+$  with  $\text{NH}_3$  (with and without direct participation of  $\text{BF}_4^-$ ). The models are visualized with the VESTA program.<sup>33</sup>

stabilization of  $17 \text{ kJ mol}^{-1}$  is achieved. In the next step, nitrosamine transforms into  $\text{HN}=\text{NOH}$ . This can be achieved without direct participation of the  $\text{BF}_3\text{-HF}$  substrate as one of the H atoms migrates from the amino group to the O atom. This requires overcoming of a very high barrier,  $126 \text{ kJ mol}^{-1}$ , as the step is slightly endothermic,  $17 \text{ kJ mol}^{-1}$ . Alternatively,  $\text{HN}=\text{NOH}$  can be formed *via* a synchronous transition state structure with the participation of the  $\text{BF}_3\text{-HF}$  substrate. Synchronously, the proton from HF migrates to the O center from the nitrosamine molecule, while one of the H atoms from the amino group migrates back to another  $\text{F}^-$  center. In this way, the process is essentially barrierless and energetically neutral. Further, there are three possibilities for the  $\text{HN}=\text{NOH}$  molecule to be transformed into  $\text{N}_2$  and  $\text{H}_2\text{O}$ : (1) migration of H from NH to the O center without participation of the  $\text{BF}_3\text{-HF}$  complex (this way was not modeled since it is expected that such a reaction step will occur with a very high barrier); (2) *via* a synchronous transition state structure where  $\text{H}_2\text{O}$  and  $\text{N}_2$  are formed in one step; (3) a concerted mechanism where in the first step,  $\text{H}_2\text{O}$  and

$\text{NNH}^+$  are formed, and afterwards,  $\text{N}_2$  is formed as the  $\text{H}^+$  migrates to the  $\text{BF}_4^-$  moiety. The second concerted mechanism is the most probable as it is essentially barrierless and highly exothermic by  $221 \text{ kJ mol}^{-1}$ .

In order to assess the favorability of  $\text{Cu(II)}$  reduction by NO in SSZ-13, we considered the reduction of  $\text{Cu}^{2+}$  located in six and eight membered rings of a CHA type zeolite structure containing two Al centers by NO (the structures are shown in Fig. 11). First, we modeled formation of a  $\text{Cu}^{2+}(\text{NO})$  complex in the zeolite, which is exothermic by  $-145$  and  $-203 \text{ kJ mol}^{-1}$ , respectively. In the second step, the complex converts to two cationic species ( $\text{Cu}^+$  and  $\text{NO}^+$ ); each of them compensates for one Al center. This step is endothermic by  $31$  and  $43 \text{ kJ mol}^{-1}$ . Thus, the overall exothermicity of the reduction of  $\text{Cu}^{2+}$  by NO to  $\text{Cu}^+$  and  $\text{NO}^+$  is  $-114$  and  $-160 \text{ kJ mol}^{-1}$ , respectively. The second reaction step seems to be also kinetically feasible, as the calculated barrier for the case of  $\text{Cu}^{2+}$  located in the six membered ring of CHA is  $62 \text{ kJ mol}^{-1}$ . These DFT results are fully consistent with our experimental findings.



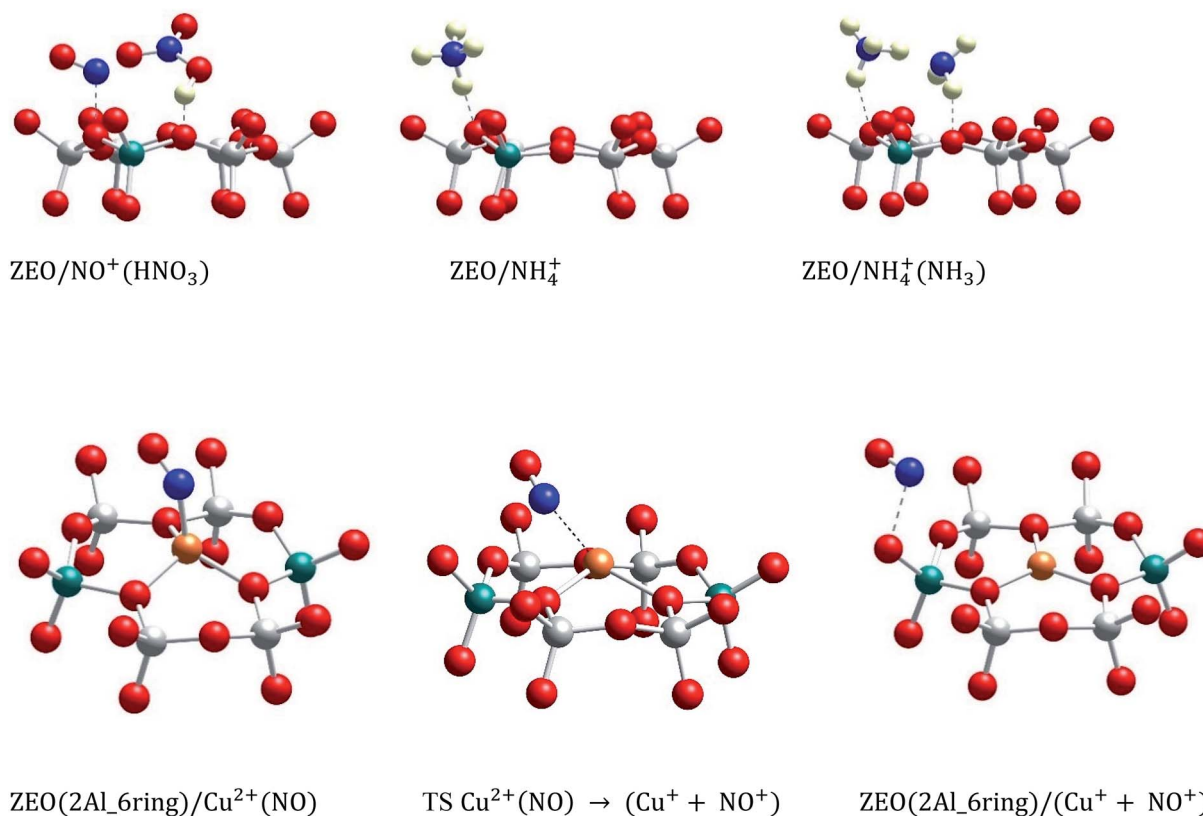
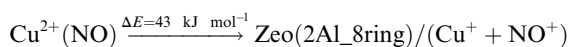
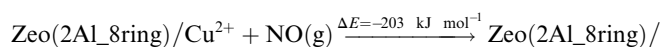
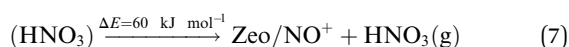
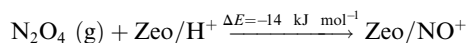
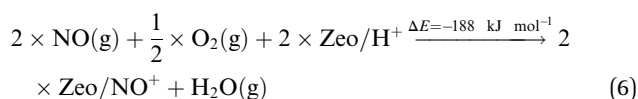


Fig. 11 Optimized structures of selected models. The models are visualized with the VESTA program.<sup>33</sup>



Additionally, we modeled the steps regarding  $\text{NO}^+$  formation and  $\text{NH}_3$  adsorption in the zeolite which are all highly favorable and exothermic. In agreement with earlier experimental studies for  $\text{NH}_3$  adsorption, interaction of  $\text{NH}_4^+$  ions with  $\text{NH}_3$  is also very favorable.<sup>24</sup>



To summarize the DFT results, we investigated two pathways for the NO reduction reaction with ammonia on both substrates (zeolite/ $\text{NO}^+$  and  $\text{BF}_4^-/\text{NO}^+$ ): (1) with and (2) without the direct participation of the substrate. When the reaction occurs on the zeolite/ $\text{NO}^+$  system with the participation of the zeolite (Fig. 7), the barriers are very low (all of them are below  $20 \text{ kJ mol}^{-1}$ ), manifesting that the reaction can occur at very low temperatures, in line with our experimental results. However, if the zeolite does not participate in the catalytic process directly, the barriers are  $>130 \text{ kJ mol}^{-1}$  (Fig. 8). According to our calculations, nitrosamine ( $\text{NH}_2\text{NO}$ ) can be formed as an intermediate (see Fig. 7), but the barrier for its transformation is very low. Similarly, the  $\text{NNH}^+$  species can be formed as well (Fig. 7), which we prove experimentally through studies with the phenyl diazonium cation (that is more stable than  $\text{NNH}^+$  shown in Fig. 4). The results with the other substrate,  $\text{BF}_4^-/\text{NO}^+$ , are similar (Fig. 10). When  $\text{NH}_3$  is decomposed with the participation of the  $\text{HF}-\text{BF}_3$  substrate, the barriers are very low, while if the substrate does not participate in the reaction directly, some of the barriers become higher than  $120 \text{ kJ mol}^{-1}$ . Similar results are also found for the aniline reduction (Fig. 9), where  $\text{PhNN}^+$



can be formed *via* the catalytic role of the zeolite as the highest barrier in the initial rate-limiting step is only 31 kJ mol<sup>-1</sup>.

Based on these combined theoretical and experimental data, we can suggest that the role of copper is to promote NO<sup>+</sup> formation since Brønsted acid sites get occupied by NH<sub>4</sub><sup>+</sup> after NO<sup>+</sup> reacts with NH<sub>3</sub> on the bare H-zeolite and cannot contribute to NO<sup>+</sup> formation as we show herein. The resulting NO<sup>+</sup> reacts with ammonia to reform N<sub>2</sub>. The Cu(I)(NH<sub>3</sub>)<sub>2</sub> complex, in turn, gets re-oxidized back to Cu(II) with oxygen.<sup>16,17</sup> Notably, this bears striking resemblance to the recent advances in enzymatic chemistry of Cu-containing enzymes for denitrification and annamox (anaerobic ammonia oxidation to nitrogen) processes. Only in recent decades, the pioneering studies of Murphy and co-workers (for denitrification)<sup>31</sup> and Kartal, Strous, and co-workers (for annamox)<sup>32</sup> revealed the central role of the Cu(I)···NO<sup>+</sup> intermediate and diazo-compounds in these processes. Our data point to the presence of a similar active site for the Cu-zeolite system (used industrially in vehicles) and Cu-enzymes, occurring in nature.

We note that our findings represent the first observation of the potential intermediates of NO reduction with ammonia (SCR) responsible for N-N bond formation for zeolites and copper-zeolite systems and lay out the strategy to investigate vehicle-relevant SCR under more complex gas feed conditions (that include water and hydrocarbons, in addition to oxygen, NO and ammonia); under these complex vehicle-relevant gas conditions, additional mechanistic pathways, leading to N-N coupling, may also be operative.

## Data availability

The data are available in the main text and the ESI.†

## Author contributions

KK conceived the project, performed most synthesis, catalytic, infra-red experiments, analyzed data and wrote the manuscript, KK and NRJ obtained funding through the QuickStarter LDRD program at PNNL. NRJ, JHK, MAD, JS performed synthesis and spectroscopy experiments, analyzed data and contributed valuable discussion. HAA, IZK, GNV performed all DFT calculations, discussed the data and co-wrote the DFT section of the manuscript. KK, MAD, NRJ, JHK, IZK, HAA, GNV, YW and JS discussed all the data and the final manuscript.

## Conflicts of interest

The authors have no conflicts to declare.

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