Understanding catalytic reactions over zeolites: A density functional theory study of selective catalytic reduction of NO\textsubscript{x} by NH\textsubscript{3} over Cu-SAPO-34 †

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Metal exchanged CHA-type (SAPO-34 and SSZ-13) zeolites are currently promising catalysts for selective catalytic reduction (SCR) of NO\textsubscript{x} by NH\textsubscript{3}. However, the understanding of above process at the molecular level is still limited, which hinders the identification of its mechanism and the design of more efficient zeolite catalysts. In this work, modelling over Cu-SAPO-34, a comprehensive periodic density functional theory (DFT) study of NH\textsubscript{3}-SCR is performed with the consideration of van der Waals (vdW) interactions. A novel N–N coupling mechanism (energy barrier 0.33 eV) with verified transition state is proposed to account for the activation of NO. The redox cycle of Cu\textsuperscript{2+} and Cu\textsuperscript{+}, which is crucial for the SCR process because O\textsubscript{2} can only be activated on the Cu\textsuperscript{+} site, is identified with detailed analysis. Besides, the decomposition of NH\textsubscript{2}NO is calculated to be readily occur on the Brønsted acid site by a hydrogen push-pull mechanism, confirming the collective efforts of Brønsted acid and Lewis acid (Cu\textsuperscript{2+}) sites. More importantly, the unique electronic and structural properties of zeolites are proved to play a essential role in all above reaction features in this study, which may have a general implication on the understanding of zeolite catalysis.

Introduction

The reduction of environmentally harmful nitrogen oxides (NO\textsubscript{x}), especially for these in lean-burn engine exhausts, is currently an important and challenging task for chemical researchers.\textsuperscript{1–4} Among possible solutions, selective catalytic reduction (SCR) of NO\textsubscript{x} by ammonia (NH\textsubscript{3}-SCR) over metal-exchanged CHA-type zeolites has attracted great attention in recent years. As the main N-containing compounds from diesel engines is NO (>90%), the main reaction of NH\textsubscript{3}-SCR can be expressed as:\textsuperscript{5}

\[
4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1)
\]

which is usually called as standard SCR. The process with equimolar mixture of NO and NO\textsubscript{2}, on the other hand, is named fast SCR that reacts much faster:\textsuperscript{6}

\[
2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 2\text{H}_2\text{O} \quad (2)
\]

Prior to zeolites, NH\textsubscript{3}-SCR techniques have been used with noble metals and metal oxides (e.g., V\textsubscript{2}O\textsubscript{5}-based catalysts) in stationary plants.\textsuperscript{7,8} However, due to the toxicity of V\textsubscript{2}O\textsubscript{5} species, the different catalytic conditions of automobiles’ engine, and the poisoning effect of sulfur species,\textsuperscript{9} zeolites have received great attention as a potential NH\textsubscript{3}-SCR catalyst and substitute of metal oxides nowadays. Among zeolites, a majority of studies in past decade were conducted on copper exchanged small-pore CHA-type zeolites (Cu-SAPO-34 and Cu-SSZ-13) because of their high NO\textsubscript{x} conversion as well as N\textsubscript{2} selectivity, non-toxicity, wider operating temperature range, and excellent hydrothermal stability in diesel engines.\textsuperscript{2–4,9}

Owing to the uniqueness of zeolite structure, the reaction mechanism of NH\textsubscript{3}-SCR differs a lot between zeolites and traditional catalysts. For example, there are two kinds of possible active sites in Cu exchanged CHA-type zeolites: the Brønsted acid (H in the zeolite framework) and Lewis acid (introduced Cu ion) site. Aiming to clarify their structure-activity relationship, lots of experiments have been carried out in this field. Korhonen et al.\textsuperscript{10} proposed that isolated Cu\textsuperscript{2+} was the active site of NH\textsubscript{3}-SCR for the first time in 2011 with operando UV-Vis spectroscopic results, and it is now widely accepted by researchers that this Cu\textsuperscript{2+} locates slightly above the six-membered ring of CHA-type zeolites in a dehydrated sample with low Cu loading.\textsuperscript{11–15} The nature of Cu species during the reaction, however, still has not been clari-
Some researchers\textsuperscript{16,17} argued that a mixture of Cu(I)–Cu(II) oxidation states will exist during standard SCR process, but it is not generally accepted yet.\textsuperscript{4} Another interesting phenomenon is that fast SCR (equation 2) reacts more rapidly than standard SCR (equation 1), of which the intrinsic reason is still under debate. Some studies\textsuperscript{18,19} suggested that in fast SCR, NO and NO\textsubscript{2} will bind in gas phase to form N\textsubscript{2}O\textsubscript{3}, followed by a hydrolysis to nitrous acid (N\textsubscript{2}O\textsubscript{3} + H\textsubscript{2}O → H\textsubscript{2}NO\textsubscript{2}). After that, N\textsubscript{3} can easily react with HONO to form NH\textsubscript{4}NO\textsubscript{2} which readily decompose to N\textsubscript{2} and H\textsubscript{2}O under reaction condition.\textsuperscript{2,9,20} In standard SCR process, NO oxidation to NO\textsubscript{2} by O\textsubscript{2} was deemed by some researchers to be the rate-limiting step, thus it is much slower than fast SCR which did not require O\textsubscript{2} to oxidise NO; however, others argued that the different reaction mechanism of fast and standard SCR was the intrinsic reason.\textsuperscript{2,4,9}

In addition to above studies, numerous investigations have been carried out on NH\textsubscript{3}-SCR over zeolites; however, several fundamental issues about its mechanism are still not well understood due to limitations of current experimental techniques on detecting dynamic and instant events at molecular level.\textsuperscript{4} Some questions remain to be answered: i) how NO is activated and what is the role of O\textsubscript{2}; ii) whether the redox cycle of Cu\textsuperscript{2+} and Cu\textsuperscript{+} is involved and what is the redox mechanism; iii) whether both Brønsted acid and Lewis acid collectively catalyse the SCR process. To elucidate these questions, several theoretical attempts have been made by Li et al.\textsuperscript{6,18} and Bruggemann et al.\textsuperscript{21,22} on H-form and Fe exchanged zeolites with finite cluster models, and some possible reaction pathways were identified. Very recently, Paolucci et al.\textsuperscript{16} proposed a detailed NH\textsubscript{3}-SCR mechanism on Cu-SSZ-13 with both operando X-ray absorption experiments and density functional theory (DFT) calculations. A Cu\textsuperscript{1+}H\textsubscript{2}N\textsubscript{2}O\textsubscript{2}/H\textsuperscript{+} and Cu\textsuperscript{1+}N\textsubscript{2}O\textsubscript{2}/NH\textsuperscript{4+} complex, according to their study, were involved in the reducing and oxidising part of the whole reaction, respectively. Despite aforementioned studies, a comprehensive first principles investigation of NH\textsubscript{3}-SCR over Cu-SAPO-34, to the best of our understanding, has not been performed yet. In this contribution, we explored the reaction by DFT calculations with the consideration of van der Waals (vdW) interactions in order to answer above three questions.

Firstly, a novel NO-assisted N–H breaking mechanism with verified transition state is proposed to account for N–N coupling process. The NO is activated by binding with N in NH\textsubscript{3} to form NH\textsubscript{2}NO while one of its N–H bond weakened. The extra H would remain at the six-membered ring of the zeolite, reducing the original Cu\textsuperscript{2+} into Cu\textsuperscript{+}. The six-membered ring of the zeolite is crucial in making this step possible, because the transition state bridges from Cu\textsuperscript{2+} to framework O, which lowers the energy barrier greatly owing to the framework flexibility of the zeolite. Then, the reduced Cu ion is able to activate O\textsubscript{2} with improved adsorption energy compared with Cu\textsuperscript{2+}; O\textsubscript{2} can thus oxidise NO into NO\textsubscript{2} with a lowered energy barrier. Moreover, during O\textsubscript{2} adsorption and NO oxidation, Cu\textsuperscript{2+} will regenerate from Cu\textsuperscript{+} to complete the Cu redox cycle. In addition, the reason why fast SCR (reaction 2) is more rapid than standard SCR (reaction 1) could also be explained by this mechanism. Finally, a detailed decomposition mechanism of NH\textsubscript{2}NO in the Brønsted acid site was conducted, confirming not only its feasibility, but also a collective efforts of Brønsted acid and Lewis acid (Cu\textsuperscript{2+}) sites in catalysing NH\textsubscript{3}-SCR over Cu-SAPO-34 over zeolites. More importantly, above findings of NH\textsubscript{3}-SCR are closely related to the unique structural and electronic properties of zeolites, including its special six-membered ring structure, influence of the framework H on the valence of loaded metal ion, collective efforts by Brønsted acid and Lewis acid sites, and confinement effects. Therefore, general implications of this work to zeolite catalysis is also discussed, which may supplement current understandings on zeolite chemistry.

Computational methods

All calculations in the paper were carried out with the Perdew–Burke–Ernzerhof (PBE)\textsuperscript{23} using the Vienna ab initio simulation package (VASP).\textsuperscript{24,25} The D3 correction method\textsuperscript{26} was employed in order to include van der Waals (vdW) interactions, which is not ignorable in zeolites due to their porous structure. The project-augmented wave (PAW) method was used to represent the core–valence interaction.\textsuperscript{27,28} For the calculations of total energy, a cut-off energy of 450 eV was set for plane wave basis sets to expand the valence electronic states and spin-polarization was included. All atoms were fully relaxed until the Hellman–Feynman forces were lower than 0.05 eV/Å. Transition states (TS) were determined by a constrained optimization scheme,\textsuperscript{29,30} in which TSs are verified until (i) all forces on atoms vanish and (ii) the total energy reaches maximum along the reaction coordination but minimum with respect to the rest of the degrees of freedom.

As we mentioned in the introduction, SAPO-34 is a specific type of silicoaluminophosphate zeolite with chabazite (CHA) structure\textsuperscript{31} whose composition of unit cell is H\textsubscript{2}Si\textsubscript{3}Al\textsubscript{6}P\textsubscript{6}O\textsubscript{24}. Experimentally, the of Si in SAPO-34 (Si/(Si+Al+P)) is usually larger than 0.1,\textsuperscript{32,33} and the value of \(x\) can be up to 1.32 as a result of magic-angle spinning NMR analysis.\textsuperscript{34,35} In our paper, we built a Cu-SAPO-34 (1 \(\times\) 1 \(\times\) 2) supercell with a \(\times\) value of 1.5 to represent the zeolite. Two H atoms were removed from the supercell to compensate the positive charge of the introduced Cu\textsuperscript{2+} ion, and the final chemical formula of the supercell is Cu\textsubscript{18}Si\textsubscript{3}Al\textsubscript{36}P\textsubscript{9}O\textsubscript{48}. Similar models have been employed by Termath et al.\textsuperscript{36} and Uzunova et al.\textsuperscript{34,37,38} This model is reasonable for investigating the NH\textsubscript{3}-SCR process since both Brønsted acid (H) and Lewis acid (Cu) are included in the supercell. During the calculations, a Monkhorst–Pack k-point sampling of 2 \(\times\) 2 \(\times\) 1 was used and the adsorption energy (\(E_{\text{ad}}\)) was defined as:

\[
E_{\text{ad}} = E_{\text{adsorbate+zeolite}} - E_{\text{adsorbate}} - E_{\text{zeolite}} \tag{3}
\]

where \(E_{\text{zeolite}}, E_{\text{adsorbate}}, \) and \(E_{\text{adsorbate+zeolite}}\) are the energies of the zeolite, adsorbate in the gas phase, and adsorbate adsorbed on the zeolite, respectively.

Results and discussion

Structure of the Cu-SAPO-34 and the adsorption of gas phase molecules

The optimized Cu-SAPO-34 supercell is displayed in Fig. 1. Under low loading content, as we mentioned in introduction, Cu was
suggested to locate slightly above the six-membered ring near two Si atoms (position 1 in Fig. 1b)\textsuperscript{2,39} as a divalent ion (Cu\textsuperscript{2+}). To validate this conclusion, we here examined the total energy of Cu-SAPO-34 when introducing Cu\textsuperscript{2+} in different positions (1–5 in Fig. 1b) and ensured that position 1 was the most stable one (Tab. S1 in ESI). We can see from the figure that Cu is coordinated with four O atoms in the six-membered ring with a distance of 2.08, 1.95, 1.91, and 2.36 Å, which is quite similar to the results in Uzunova et al.'s papers.\textsuperscript{34,37,38} There are two Si atoms in the ring, while the remaining Si is accompanied by a H atom to form the Brønsted acid site. The stability of different H positions (1–4 in Fig. 1a) were also tested. Position 1–4 show a very close total energy, among which position 1 is slightly preferable (Tab. S2 in ESI). Lastly, the volume of the relaxed supercell was calculated to be 1662.5 Å\textsuperscript{3}, very close to the experimental value (1644.8 Å\textsuperscript{3}).\textsuperscript{35,40}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{Structural illustrations of the (a) Cu-SAPO-34 supercell; (b) periodic view of the elliptical circle in (a). Green, red, purple, yellow, brown, and white balls represent P, O, Al, Si, Cu, and H atoms, respectively. This notation will be used throughout the paper.}
\end{figure}

From reaction equation (1) and (2), we know that the reactants of SCR are NH\textsubscript{3}, NO, O\textsubscript{2}, and NO\textsubscript{2} (possibly with a small portion of water). We subsequently investigated their adsorption on both Brønsted acid (B-site) and Lewis acid (L-site) sites, best adsorption configurations of which are illustrated in Fig. 2. It is clear from Fig. 2 that both NO\textsubscript{2} and H\textsubscript{2}O exhibit a moderate adsorption on B- and L-sites, while O\textsubscript{2} hardly resides over the zeolite. NO prefers to bind the Cu\textsuperscript{2+} ion by its N end and showed a strong $E_{\text{ad}}$ of -1.29 eV, yet its adsorption on B-sites is relatively weak. NH\textsubscript{3} has a solid bonding on both sites, and it will exist in a NH\textsubscript{4}\textsuperscript{+} form on B-sites. The results indicate that L-sites will be dominantly covered by NH\textsubscript{3} and NO at the start of SCR process, and the B-site by NH\textsubscript{3}. It is in accordance with the generally accepted opinion that NH\textsubscript{3} and NO shall react on L-sites whereas B-sites sever as a NH\textsubscript{3} reservoir in the beginning of the reaction.\textsuperscript{4,41} The NH\textsubscript{3} in B-sites will migrate to L-sites as reactions proceeds.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig2.png}
\caption{Structural illustration of the adsorption of NH\textsubscript{3} (ab), NO (cd), O\textsubscript{2} (ef), NO\textsubscript{2} (gh), and H\textsubscript{2}O (ij). The left and right columns refer to the Brønsted acid (H) and Lewis acid (Cu\textsuperscript{2+}) site, respectively.}
\end{figure}

**Initial coupling of the N–N bond**

The full mechanism of NH\textsubscript{3}-SCR is considerably complicated.\textsuperscript{3,9} Among that, N–N coupling is a crucial step towards the formation of nitrogen; therefore, it will be firstly considered in this paper. Considering the valence of N, the coupling two N atoms shall come from NH\textsubscript{3} and NO, respectively. According to this principle, we tried plenty of possible attacking manners of NO to NH\textsubscript{3} in or-
nder to form N–N bond, but all the them failed. A huge resistance would occur when N in NO approaches NH$_3$; the NO would be pushed away if we force them to be close. It is reasonable since N in the binding NH$_3$ is saturated (Fig. 2a). Therefore, the possibility of direct attacking of NO to NH$_3$ is ruled out. Then, in order to circumvent the problem of the saturated NH$_3$, we alternatively tried to remove one H from the NH$_3$ to form NH$_2$ because NH$_2$ is unsaturated, which would be easier for NO to react. Five positions indicated in Fig. 2a were considered to be resided by H after NH$_3$ decomposition. However, from the results in Fig. S1, we found that all these pathways are extremely unfavourable in thermodynamics; the total energies of them is 0.76–1.76 eV higher than that in Fig. 2a, let alone their kinetic barriers. So, it would be very difficult to directly remove one H from NH$_3$. On traditional NH$_3$-SCR catalysts (e.g. MnO$_2$ and V$_2$O$_5$), it is possible for NH$_3$ to donate one H to surface O with a reasonable barrier, but such a pathway is not practical here since the H accepting ability of zeolite framework is inferior to that of oxides.

Aiming to find a reasonable pathway for N–N bonding on NH$_3$-SCR over Cu-SAPO-34, we here propose a NO-assisted mechanism along with NH$_3$ dehydrogenation:

$$\text{NH}_3 + \text{NO} + Z \rightarrow \text{NH}_2\text{NO} + Z - \text{H} \quad (4)$$

where Z indicates the zeolite. The main idea of the mechanism is that when NO is approaching NH$_3$ to form N–N bond, one N–H bond in NH$_3$ will weaken as its H comes close to the framework oxygen of the six-membered ring. We subsequently investigated relevant intermediates and transition states of the reaction, whose structures and energies are displayed in Fig. 3.

From the figure, we found that NO and NH$_3$ would adsorb on the Cu$^{2+}$ with considerable adsorption energies (more than 1 eV). It is worth noting that in the insert (ON-Z-NH$_3$) of Fig. 3, the distance between of one H in the NH$_3$ is quite close to a framework O (1.78 Å), indicating a hydrogen bond interaction between them. Then, in the transition state, NH$_3$ would approach the framework O, intending to bond it with the H. The distance between two N atoms, at the same time, would shorten to a certain level (1.58 Å). Finally, since the bonding of two N would release lots of energy that compensating the energy needed to break the N–H bond in NH$_3$, two N atoms couple to form NH$_2$NO while the H remains on the framework O (insert H-Z-NH$_2$NO in Fig. 3). The energy barrier for this process was calculated to be 0.33 eV, an exceptionally small value which means reaction 4 a very effective way to activate the NO in NH$_3$-SCR. To the best of our knowledge, such a transition state in this system is for the first time been proposed, and we further made a frequency analysis to ensure its accuracy. The results showed that the transition state here exhibited one and only one imaginary frequency, which corresponds to N–N coupling and N–H breaking with a value of 450.5 i cm$^{-1}$. The NH$_2$NO would transfer to B-sites for further decomposition, which will be demonstrated in detail the last subsection. In addition, we made a Bader analysis towards Cu ion before (Z) and after (Z-H) N–N coupling reaction, finding that the valence of Cu ion changed from 1.12 to 0.69 which meant that Cu$^{2+}$ partly reduced to Cu$^+$. The result is quite reasonable, since we can see from the left column of Fig. 2 and schemes in Fig. 3 that before N–N coupling, Cu$^{2+}$ ion tend to coordinate with four atoms, while the coordination number of Cu$^+$, after the reaction, becomes two (scheme H-Z-NH$_2$NO in Fig. 3). The phenomena agree well with the common sense in coordination chemistry.

We will have a deep insight into the valence change of Cu ion and the intrinsic reason why the reaction can happen over zeolites by such an low-energy-barrier mechanism in the discussion section.
NO and Cu\(^{2+}\) oxidation by O\(_2\)

Although the whole reaction is the reduction of NO\(_x\), O\(_2\) plays a crucial role in the SCR process.\(^4,9\) Some researchers argued that in standard SCR O\(_2\) will oxidise NO into NO\(_2\), resulting a fast SCR; however, more studies in recent years showed that standard and fast SCR may exhibit distinct mechanisms.\(^4,5\) Currently, a clear mechanism for NO oxidation to NO\(_2\) on the Cu ion is under debate and have not been achieved yet. Some previous studies stated that NO was oxidised by O\(_2\) in the gas phase or in pores of zeolites (O\(_2\) + 2NO \(\rightarrow\) 2NO\(_2\)),\(^18\) but it is a three-molecule reaction thus its contribution to the overall NO oxidation is limited. We suggest that the elementary reaction here is

\[
\text{O}_2 + \text{NO} + \text{Z}-\text{H} \rightarrow \text{NO}_2 + \text{O} - \text{Z}-\text{H} \quad (5)
\]

where the metal ion sites play the main role. Z-H in equation 5 means that a H resides on the framework O of the six-membered ring (Fig. S2a). It should be noted that NH\(_3\) has a strong inclination to adsorb on this H site (\(E_{\text{ad}} = -1.66\) eV), forming NH\(_4^+\) on the ring (Z-NH\(_4\), Fig. S2b). Then, we investigated the adsorption of O\(_2\) on Cu ion site as well as the energy barriers and total energy change of above reaction, the results are listed in Tab. 1.

<table>
<thead>
<tr>
<th>(E_{\text{ad}}) of O(_2)</th>
<th>Energy barriers</th>
<th>Total energy change</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>co-adsorb</td>
<td>gas phase</td>
</tr>
<tr>
<td>Z</td>
<td>-0.19</td>
<td>1.40</td>
</tr>
<tr>
<td>Z-H</td>
<td>-0.58</td>
<td>0.92</td>
</tr>
<tr>
<td>Z-NH(_3)</td>
<td>-0.62</td>
<td>0.86</td>
</tr>
</tbody>
</table>

From the table, we find that O\(_2\) hardly adsorbs on Z, i.e., Cu\(^{2+}\) site (\(E_{\text{ad}} = -0.19\) eV, Fig. 2e), which agrees well with the former conclusion that Cu\(^{2+}\) ions are incapable of activating O\(_2\).\(^4,6\) However, after N–N coupling, Cu\(^{2+}\) has been reduced to Cu\(^+\) with a H on the six-membered ring (Z-H), on which the adsorption energy of O\(_2\) increased considerably (\(E_{\text{ad}} = -0.58\) eV, Fig. S2c). In addition, NH\(_3\) can readily adsorb on the H atom to form Z-NH\(_4\) (Fig. S2b), which adsorbs O\(_2\) with similar capacity (\(E_{\text{ad}} = -0.62\) eV, Fig. S2d). It seems that the reduction of Cu ion will help O\(_2\) activation and subsequently facilitate the overall NO oxidation process, and we further explored reaction energy barriers over different sites. Two kinds of attacking manner of NO to O\(_2\)—gas phase and co-adsorbing site—were considered, the results of which were shown in Tab. 1, Fig. 4, and Fig. S3.

Over Z-H, we found that the NO and O\(_2\) co-adsorbing initial state (right column in Fig. 4) is more favourable for NO oxidation than NO attacking from the gas phase (left column in Fig. 4); their respective energy is 0.92 eV and 1.18 eV. Similar trend were also find in Z-NH\(_3\) (Fig. S3) where energy barrier for catalysing this reaction is slightly lower (0.86 eV, Tab. 1) than Z-H. However, the energy barrier for NO oxidation is very high in Z (1.40 eV for co-adsorbing initial state), and a transition state cannot even be found if NO is attacking from the gas phase. With these evidence, we can safely conclude that the reduction of Cu ion will facilitate NO oxidation on this site. After that, the produced NO\(_2\) can react with its neighbouring NH\(_4^+\) (Fig. S3f or Fig. 4f with NH\(_3\) adsorption) to form NH\(_4^+\)NO\(_2\), leaving an O over the zeolite. Eventually, the NO oxidation reaction over Cu-SAPO-34 zeolites can be expressed as follows:

\[
\text{O}_2 + \text{NO} + \text{NH}_3 + \text{Z}-\text{H} \rightarrow \text{NH}_4\text{NO}_2 + \text{Z} - \text{O} \quad (6)
\]

It is well recognized that NH\(_4\)NO\(_2\) is easy to stoichiometrically decompose into N\(_2\) and H\(_2\)O under SCR operation condition;\(^2,4,9,20\)

\[
\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \quad (7)
\]

Furthermore, we tested the bader charge of Cu in Z-O, finding its valence resumed to 1.21, which indicated that Cu\(^+\) was oxidised back to Cu\(^{2+}\). To sum up, reaction 4 and 5 not only couple the N–N bond and form NH\(_3\)NO and NH\(_4\)NO\(_2\), but also consist a redox cycle. Intuitively, the involvement of a redox cycle is quite reasonable because from equation 4 and 6, we can see that the reaction ratio of NH\(_3\) and NO is 1:1, while the oxidation states of N in them is a mismatch (-3 in NH\(_3\) and +2 in NO). Therefore, the coupling of N–N bond in NH\(_3\) and NO must be accompanied by the reduction of L-site (Cu\(^{2+}\) \(\rightarrow\) Cu\(^+\)) which will regenerate by the oxidation of O\(_2\). The redox cycle well explains the experimental observation that steady state NO conversion would decrease to zero after O\(_2\) cut-off under standard SCR condition.\(^16\) According to their study, the content of Cu\(^+\) increases to 75–95% of the whole Cu species, and SCR reactions would be soon stuck since N–N coupling cannot happen on Cu\(^+\) site.
If we consider fast SCR (reaction 2) in which NO$_2$ directly involved, NO oxidation is not necessary after N–N coupling and the reaction goes as follows:

\[ \text{NO}_2 + \text{NH}_3 + \text{Z} - \text{H} \rightarrow \text{NH}_4\text{NO}_2 + \text{Z} \quad (8) \]

NO$_2$ and NH$_3$ can strongly adsorb on Cu$^+$ and framework H site ($E_{ad} = -1.32$ and $-1.66$ eV in Fig. S2e and S2b, respectively), and NO$_2$ would naturally get together with its neighbouring NH$_4^+$ to form NH$_4$NO$_2$ (Fig. S2f). Interestingly, the fast SCR will not go through the energy barrier for NO oxidation (0.86 eV) which is the highest among all elementary reactions in our paper. It may explain the main reason why fast SCR reacts more rapid than standard SCR.

**NH$_4$NO formation after oxidation**

After the oxidation by O$_2$, the copper restores to Cu$^{2+}$ and the rest of reactions are quite intuitive (aiming to the formation of NH$_4$NO), the reactions of which can be expressed as follows:

\[ \text{NH}_3 + \text{Z} - \text{O} + \text{NO} \rightarrow \text{NH}_2\text{NO} + \text{Z} - \text{OH} \quad (9) \]

\[ \text{NH}_3 + \text{NO} + \text{Z} - \text{OH} \rightarrow \text{NH}_2\text{NO} + \text{H}_2\text{O} + \text{Z} \quad (10) \]

The proposed reaction mechanism and their energy profile are illustrated in Fig. 5.

**Fig. 5 Total energy profile and structural illustration of reaction 9 (a) and 10(b)**

For reaction 9 (Fig. 5a), NH$_3$ in the gas phase or B-site reservoir would adsorb on the Z-O with a strong adsorption of -1.32 eV. Then, one of the H in NH$_3$ transferred to Z-O, forming HO-Z-NH$_2$ with a moderate energy barrier of 0.62 eV. Subsequently, the unsaturated NH$_2$ is would easily couple with NO in the pores of zeolites to form NH$_2$NO with a considerable energy decline. Finally, NH$_2$NO would transfer to B-site for further decomposition, leaving OH group on the six-membered ring. Reaction 10 (Fig. 5b) processes very similar to reaction 9. After adsorbing a NH$_3$ molecule, H transfers from NH$_3$ to OH (0.66 eV), and NO bonds with remaining NH$_3$ to form the last NH$_2$NO. It is worth noting that on above processes, the following Eley-Rideal reaction is barrierless:

\[ \text{NH}_2 + \text{NO} \rightarrow \text{NH}_2\text{NO} \quad (11) \]

With an unpaired electron in the N side of NO ($\pi^*$) and unsaturated $p$ orbital of NH$_2$ respectively, NO and NH$_2$ are extremely preferred to link together to form N–N bond, with considerable energy release (over 1.5 eV). Also, due to the confinement effect of zeolites, the possibly of molecule collision in cages of zeolites increased a lot. Therefore, it would be much easier for such an Eley-Rideal reaction to occur.

**NH$_4$NO decomposition into H$_2$O and N$_2$**

Finally, the NH$_4$NO formed in above stages will decompose into H$_2$O and N$_2$ to complete the whole SCR process. Many previous studies showed it a relatively easily process in the B-site of zeolites by a hydrogen push-pull mechanism.\textsuperscript{18,21} We here investigated its decomposition on both Brønsted acid and Lewis acid site, finding that the Brønsted site is indeed more favourable, and all intermediates and transition states were identified (Fig. S5).

It can be seen from the scheme in Fig. 6 that the configuration of NH$_2$NO will change several times by the transferring of H atom, which was well recognised by previous studies.\textsuperscript{18,49} We firstly tried this process on the L-site (Fig. S4), but the energy barrier of the first step of NH$_2$NO decomposition in L-acid, the proton transferring from N to O, was extremely high (2.11 eV). From Fig. S4b, we can see that during intra-molecular proton transfer, an unstable four-membered ring is formed, exerting a strong steric hindrance and make L-side unfavourable for catalysing this reaction. On the other hand, energy barriers of the reactions on B-site are moderate, making it easy to occur (energy profile in Fig. 6, and corresponding structures in Fig. S5).

As shown in Fig. S5a, NH$_2$NO adsorbs on the B-site by the interaction between O and H atoms. The B-site here serves as a H reservoir, helping NH$_2$NO to transfer H by the so-called hydrogen push-pull mechanism. So, in the subsequent steps, NH$_2$NO transforms its configuration for several times by donating and receiving H with the help of the framework and finally decomposes to N$_2$ and H$_2$O with considerable energy plunge. The highest effective barrier for NH$_2$NO decomposition is 0.81 eV (from NH$_2$NO to TS2), which is much lower than that in L-site and has a reasonable reaction rate under typical SCR condition (ca. 450–500 K). The results show that Bronsted acid and Lewis acid (Cu$^{2+}$) sites would collectively catalyse NH$_3$-SCR over Cu-SAPO-34 zeolites.

**Overall mechanism**

An overall picture of NH$_3$-SCR over Cu-SAPO-34 is schematically illustrated in Fig. 7. From the figure, we can find that the mechanism of standard SCR is rather complicated, which is reasonable since the reaction involves totally nine molecules of react-
General discussion of the zeolite chemistry

In recent years, zeolites have been widely used in the fields petrochemical industry, fine chemicals, and other heterogeneous reactions. As a crystalline microporous material, zeolites own plenty of novel properties in species migration, ion exchange, adsorption, etc., which give us more efficient and cheap alternatives for some traditional catalysts. The relation between unique properties of Cu-SAPO-34 zeolites and activities of SCR process, however, has not been well understood yet. We therefore make a general discussion about its structure-activity relationship in this subsection, aiming to supplement current understandings on zeolite chemistry.

Starting from an isolated Cu$^{2+}$ ion, the first step of SCR is the N–N coupling between NO and NH$_3$ that goes through an exceptionally small barrier (0.33 eV) as we stated in the results. One question naturally arises here: why NO can be activated by such a low-energy-barrier way? The origin lies in the special zeolites’ structure. In our model, diameter of the six-membered ring is about 5~6 Å, and the structure of transition state (scheme TS in Fig. 3) fits such a ring well upon N–N coupling; the whole molecule (NH$_2$NO) bridges from Cu ion to a framework O with a quite reasonable structure. One of H in the NH$_3$ will interact with the framework O with the hydrogen bond, thus lowering the total energy of the transition state. Meanwhile, the six-membered ring will also stretch to some extent to fit the structure of transition states owing to the flexibility of zeolite framework. Moreover, the weakened N–H bond of the transition state also provides its N more rooms to couple with another N. These unique features of zeolites may partly explain their good performance on catalysing NH$_3$-SCR, and such a NO-assisted N–N coupling mechanism in NH$_3$-SCR could be extended to other zeolite systems (e.g., SSZ-13 or ZSM-5).

Then, we shall have a deep insight into the redox cycle in its mechanism. From Fig. 7, we can notice that the valence of Cu ion in Cu–NH$_2$NO/H, Cu/H, and Cu/NH$_3$ are +1 while in the rest species are +2 (measured by bader charge analysis, details in Tab. S3). The redox cycle is very important in the whole SCR process.
process especially for standard SCR, since Cu$^{2+}$ is not able to activated O$_2$ molecules and the involvement of Cu$^{+}$ is crucial for NO oxidation according to the results in last section. Aiming to clarify the role of zeolites in such a redox cycle, we calculated the valence number of the whole six-membered ring of Cu$^{2+}$ and Cu$^{+}$ (Fig. 8ab). In Fig. 8b, one H remains on the framework O after N–N coupling, and its electron will entirely transfer to the framework (its valence becomes +1.00). Then, comparing atoms in the six-membered ring in Fig. 8ab, P, Al, and Si atoms are found to be incapable of holding the extra electron donated by H, and O can capture about 0.1 electrons per atom. Consequently, a significant amount of electrons are gathered by Cu$^{2+}$ ion which is reduced to Cu$^{+}$. Moreover, isosurfaces of charge density difference before and after O$_2$ adsorption on these two Cu site are presented in Fig. 8cd. It is clear from Fig. 8c that the electronic interaction between O$_2$ molecule and Cu$^{2+}$ is very limited, because it is hard for Cu$^{2+}$ to donate electrons on its highest oxidation state. On the other hand, Cu$^{+}$ interacts with O$_2$ well by electron accumulation on O$_2$ and depletion on Cu$^{+}$. According to bader charge analysis, the valence of Cu and two O atoms in Fig. 8 are 1.01, -0.25, and -0.1, respectively, indicating that 0.35 electrons are donated from Cu ion and the framework to O$_2$, and Cu$^{+}$ resumes to Cu$^{2+}$ accordingly. Therefore, the adsorption energy of O$_2$ increased from -0.19 on Cu$^{2+}$ to -0.62 eV on Cu$^{+}$. More importantly, the O–O bond in the O$_2$ molecule will be activated upon adsorption on Cu$^{+}$, leading to a lower energy barrier for NO oxidation.

In addition to the Lewis acid site (Cu ion), the last part of SCR process, the decomposition of NH$_2$NO, occurs on the Brønsted acid site with moderate energy barriers. It means that Brønsted acid and Lewis acid sites collectively catalyse the reaction, which is also a special feature for zeolites. In short, the adsorption of NO is weak on Brønsted acid sites while Lewis acid sites can well accommodate NO and NH$_3$ for subsequent N–N coupling reaction; besides, NH$_2$NO is hard to decompose on Lewis acid sites due to a large intra-molecular proton transfer barrier, while Brønsted acid sites can facilitate this process by a hydrogen push-pull mechanism. Such a "multi-site" concept of catalysis is receiving increasingly attention in recent years.\textsuperscript{53,54}

**Conclusion**

In this work, a comprehensive investigation of NH$_3$-SCR process over Cu-SAPO-34 zeolites were carried out by virtue of periodic DFT calculations with the consideration of van der Waals (vdW) interactions, the main conclusions of which are:

- A detailed step-by-step NH$_3$-SCR mechanism over Cu-SAPO-
were proposed with moderate energy barriers and reasonable intermediate structures.

- A novel NO-assisted N–H bond breaking mechanism N–N with verified transition state was proposed to account for N–N formation process.

- The NO oxidation by O$_2$ was proved to occur on reduced Cu site (Cu$^+$), and the Cu$^+$ will resume to Cu$^{2+}$ after oxidation, completing the Cu$^{2+}$/Cu$^+$ redox cycle.

- A detailed decomposition mechanism of NH$_3$NO in the Brønsted acid site is identified, confirming not only its feasibility, but also a collective efforts of Brønsted acid and Lewis acid (Cu$^{2+}$) sites in catalysing NH$_3$-SCR over Cu-SAPO-34 zeolites.

More importantly, above conclusions of the reaction is closely related to the unique structural and electronic properties of zeolites, including its special six-membered ring structure, influence of the framework H on the valence of loaded metal ion, collective efforts by Brønsted acid and Lewis acid sites, and confinement effects. These features may extend to more general catalytic reactions over zeolites and would supplement current understandings on zeolite chemistry.

Acknowledgements

This work was supported by the Science Fund of Creative Research Group (21421004), National Natural Science Foundation of China (21333003, 21303052), Shanghai Rising-Star Program (13CG24), the Commission of Science and Technology of Shanghai Municipality (12ZR1442600), Fundamental Research Funds for the Central Universities, including its special six-membered ring structure, influence of the framework H on the valence of loaded metal ion, collective efforts by Brønsted acid and Lewis acid sites, and confinement effects. These features may extend to more general catalytic reactions over zeolites and would supplement current understandings on zeolite chemistry.

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