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## **Understanding catalytic reactions over zeolites: A density functional theory study of selective catalytic reduction of NOX by NH3 over Cu-SAPO-34**

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## Article

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# Understanding catalytic reactions over zeolites: A density functional theory study of selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> over Cu-SAPO-34

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## Abstract

Metal exchanged CHA-type (SAPO-34 and SSZ-13) zeolites are promising catalysts for selective catalytic reduction (SCR) of  $\text{NO}_x$  by  $\text{NH}_3$ . However, the understanding of the 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 the reaction over Cu-SAPO-34, a periodic density functional theory (DFT) study of  $\text{NH}_3$ -SCR was performed using hybrid functional with the consideration of van der Waals (vdW) interactions. A mechanism with a low N–N coupling barrier is proposed to account for the activation of NO. The redox cycle of  $\text{Cu}^{2+}$  and  $\text{Cu}^+$ , which is crucial for the SCR process, is identified with detailed analyses. Besides, the decomposition of  $\text{NH}_2\text{NO}$  is shown to readily occur on the Brønsted acid site by a hydrogen push-pull mechanism, confirming the collective efforts of Brønsted acid and Lewis acid ( $\text{Cu}^{2+}$ ) sites. The special electronic and structural properties of Cu-SAPO-34 are demonstrated to play an essential role the reaction, which may have a general implication on the understanding of zeolite catalysis.

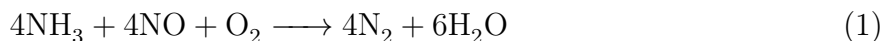
## Keywords

Density functional theory, Selective catalytic reduction, Cu-SAPO-34, Ammonia, Zeolite, Nitric oxide

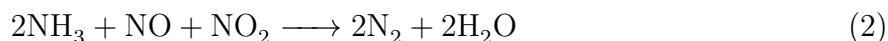
## Introduction

The reduction of environmentally harmful nitrogen oxides ( $\text{NO}_x$ ), especially for these in lean-burn engine exhausts, is currently an important and challenging task for chemical researchers.<sup>1–4</sup> Among possible solutions, selective catalytic reduction (SCR) of  $\text{NO}_x$  by ammonia ( $\text{NH}_3$ -SCR) over metal-exchanged CHA-type zeolites has attracted great attention in recent years. As the major N-containing compounds from diesel engines is NO (>90%), the

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3 main reaction of NH<sub>3</sub>-SCR can be expressed as:<sup>5</sup>  
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10 which is usually called the standard SCR. The process with equimolar mixture of NO and  
11 NO<sub>2</sub>, on the other hand, is named the fast SCR that reacts much faster:<sup>6</sup>  
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20 Prior to zeolites, NH<sub>3</sub>-SCR techniques have been used with noble metals and metal oxides  
21 (*e.g.*, V<sub>2</sub>O<sub>5</sub>-based catalysts) in stationary plants.<sup>7-9</sup> However, due to the toxicity of V<sub>2</sub>O<sub>5</sub>  
22 species and different catalytic conditions of automobile engines,<sup>10</sup> zeolites have received  
23 great attention as potential NH<sub>3</sub>-SCR catalysts nowadays. Among all zeolites, a majority of  
24 studies in past decade were conducted on copper exchanged small-pore CHA-type zeolites  
25 (Cu-SAPO-34 and Cu-SSZ-13) because of their high NO<sub>x</sub> conversion as well as high N<sub>2</sub>  
26 selectivity, non-toxicity, wider operation temperature ranges, and excellent hydrothermal  
27 stability in diesel engines.<sup>2-4,10-12</sup> Cu-SSZ-13 is now in commercial use<sup>13</sup> and received much  
28 attention in past several years; SAPO-34 has the same topology with SSZ-13, but with  
29 different silica ratio. Kwak *et al.*<sup>14</sup> demonstrated that Cu-SSZ-13, compared with Cu-beta  
30 and Cu-ZSM-5, was more active in SCR over the entire temperature range and more selective  
31 towards nitrogen formation (less NO<sub>2</sub> and N<sub>2</sub>O by-products). Ma *et al.*<sup>15</sup> reported that Cu-  
32 SAPO-34 would be more active than Cu-SSZ-13 after hydrothermal treating.  
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47 There are two kinds of possible active sites in Cu exchanged CHA-type zeolites: the  
48 Brønsted acid (H in the zeolite framework) and Lewis acid (introduced Cu ion) sites. For  
49 the Cu sites, diffuse reflectance infrared fourier transform (DRIFT) spectroscopy and X-ray  
50 absorption spectroscopy (XAFS) showed that they would locate in both six- and eight-  
51 membered ring.<sup>12,16-18</sup> Catalytic experiments of Beale *et al.*<sup>19</sup> revealed that the mononuclear  
52 Cu<sup>2+</sup> in six-membered rings is responsible for N<sub>2</sub> production, while the Cu in eight-membered  
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3 ring ( $\text{CuAlO}_2$ ) appears to promote the formation of undesired  $\text{N}_2\text{O}$ . They pointed out that  
4 the SCR activity is inexorably linked with isolated Cu on the six-membered ring. DFT  
5 calculations also indicated that isolated Cu ions prefer to lie slightly above the six-membered  
6 ring of CHA-type zeolites.<sup>20–28,25,29–32</sup> When Cu loading is high, Cu dimers would be formed  
7 in the zeolites,<sup>33</sup> yet they may not be directly related with SCR reactivity.<sup>11</sup> Xue *et al.*<sup>34</sup>  
8 reported that the TOF value of SCR would be a function of isolated  $\text{Cu}^{2+}$  amount over  
9 Cu-SAPO-34. For Brønsted acids, it is currently not well understood what role it is in  
10 reaction system. Some studies showed that the Brønsted acid site could catalyse part of the  
11 reaction,<sup>6,35,36</sup> while others argued that its effect is rather limited.<sup>11,25,37</sup>

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13 The nature of Cu species during the reaction is more complicated. According to the  
14 latest research of Schneider *et al.*<sup>12</sup> the oxidation state and coordination environment of  
15 Cu would vary as a function of environmental conditions. For example, upon adsorption of  
16  $\text{NH}_3$ , NO, or  $\text{H}_2\text{O}$  on the Cu atoms in six-membered ring, the Cu atoms may be lift out from  
17 their original position into the larger cavities to form Cu complexes,<sup>38–40</sup> such as  $\text{Cu}(\text{H}_2\text{O})_6$   
18 and  $\text{Cu}(\text{NH}_3)_6$ .<sup>16,25,33,41,42</sup> But only Cu sites near six-membered rings seem to contribute to  
19 SCR activity in CHA-type zeolites.<sup>19,24,25,43</sup> Furthermore, many studies<sup>11,23,28,44,45</sup> suggested  
20 that a mixture of Cu(I)–Cu(II) oxidation states co-exist during the standard SCR, and the  
21 SCR process will be accompanied by a redox cycle of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$ . Initially,  $\text{Cu}^{2+}$  in  
22 the zeolites would be reduced to  $\text{Cu}^+$  by the adsorption of NO and  $\text{NH}_3$  to form  $\text{N}_2$  and  
23  $\text{H}_2\text{O}$ .<sup>28,46,47</sup> NO oxidation then takes place on the  $\text{Cu}^+$  site, regenerating  $\text{Cu}^{2+}$  that completes  
24 the redox cycle.<sup>11,28</sup> The presence of  $\text{Cu}^+$  was identified by many experimental investigations,  
25 including X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR).<sup>23,25,34,44,48</sup>

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27 Furthermore, the reaction rate of fast SCR (equation 2) is much higher than the standard  
28 SCR (equation 1), the intrinsic reason of which is still under debate. Most studies suggested  
29 that in the standard SCR process, NO oxidation to  $\text{NO}_2$  by  $\text{O}_2$  is the rate-limiting step,<sup>11</sup>  
30 and thus it is much slower than fast SCR which did not require  $\text{O}_2$  to oxidise NO. For  
31 example, Janssens *et al.*<sup>11</sup> proposed that NO and  $\text{O}_2$  would react on the  $\text{Cu}^+$  site to form  
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4  $\text{NO}_3^-$ , which would further react with NO to produce  $\text{NO}_2^-$  and  $\text{NO}_2$ . In the fast SCR, NO  
5 and  $\text{NO}_2$  could also bind in the gas phase to form  $\text{N}_2\text{O}_3$ , followed by a hydrolysis to nitrous  
6 acid ( $\text{N}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow 2 \text{HONO}$ ).<sup>36,49</sup> After that,  $\text{NH}_3$  can easily react with HONO to  
7 form  $\text{NH}_4\text{NO}_2$  that decomposes readily to yield  $\text{N}_2$  and  $\text{H}_2\text{O}$  under reaction conditions.<sup>2,10,15</sup>  
8 Tronconi *et al.*,<sup>50</sup> however, challenged this explanation using the experimental observation  
9 that rate of NO oxidation over zeolites is much slower than the standard SCR.  
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16 In addition to above studies, numerous investigations have been carried out on  $\text{NH}_3$ -SCR  
17 over zeolites; however, several fundamental issues about its mechanism are still not well  
18 understood due to the limitations of current experimental techniques on detecting dynamic  
19 and instant events at the molecular level.<sup>4</sup> The large number of possible reactions in SCR  
20 system also makes reaction pathways very complicated. Some important questions remain to  
21 be answered: (i) how NO is activated and what the role of  $\text{O}_2$  is; (ii) whether the redox cycle  
22 of  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  is involved and what the redox mechanism is; (iii) whether both Brønsted  
23 acid and Lewis acid collectively catalyse the SCR process. To elucidate these questions,  
24 several theoretical attempts have been made by Li *et al.*<sup>6,36</sup> and Bruggemann *et al.*<sup>35,51</sup> on  
25 H-form and Fe exchanged zeolites with cluster models, and some possible reaction pathways  
26 were identified. Paolucci *et al.*<sup>28</sup> proposed a detailed  $\text{NH}_3$ -SCR mechanism on Cu-SSZ-13  
27 using both operando X-ray absorption experiments and density functional theory (DFT)  
28 calculations.  $\text{Cu}^{\text{I}}\text{H}_2\text{NNO}/\text{H}^+$  and  $\text{Cu}^{\text{II}}\text{NO}_2/\text{NH}_4^+$  complexes, according to their study, were  
29 involved in the reducing and oxidising parts of the whole reaction, respectively. Very re-  
30 cently, Janssens *et al.*<sup>11</sup> proposed a consistent scheme of  $\text{NH}_3$ -SCR over Cu-SSZ-13. They  
31 described a complete catalytic cycle with correct stoichiometry while allowing adsorption and  
32 desorption of stable molecules only. Despite aforementioned studies, a comprehensive first  
33 principles investigation of  $\text{NH}_3$ -SCR over Cu-SAPO-34, to the best of our knowledge, has not  
34 been performed yet. In this contribution, we explore the reaction by DFT calculations with  
35 hybrid (HSE06) functional to answer above three questions. Van der Waals (vdW) interac-  
36 tions were also included to accurately describe the system. A detailed step-by-step  $\text{NH}_3$ -SCR  
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4 mechanism over Cu-SAPO-34 were obtained with moderate energy barriers and reasonable  
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6 intermediate structures. Our results show that the high activity of zeolites on catalysing  
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8  $\text{NH}_3$ -SCR are closely related to their structural and electronic properties, including special  
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10 six-membered ring structure, influence of the framework H on the valence of loaded metal  
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12 ion, and collective efforts by Brønsted acid and Lewis acid sites. Our study extends beyond  
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14 what have been published on SSZ-13, providing both insight into SCR catalysts and zeolite  
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16 chemistry.

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All calculations in the paper were carried out with the Heyd–Scuseria–Ernzerhof (HSE06) functional<sup>52–54</sup> using the Vienna ab initio simulation package (VASP).<sup>55,56</sup> The D3 correction method<sup>57</sup> was employed in order to include van der Waals (vdW) interactions, which may not be ignorable in zeolites due to their porous structure. The project-augmented wave (PAW) method was used to represent the core–valence interaction.<sup>58,59</sup> For the calculations of total energy, a cut-off energy of 400 eV was set for plane wave basis sets to expand the valence electronic states and spin-polarization was included. Transition states (TS) were determined by a constrained optimization scheme,<sup>60,61</sup> 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. For computational efficiency, the geometrical optimization was firstly calculated by Perdew–Burke–Ernzerhof (PBE) functional;<sup>62</sup> all atoms were fully relaxed until the forces were lower than 0.05 eV/Å. Then HSE06 functional was employed to obtain the accurate total energy. To obtain the free energy of species, some standard formulas of statistical mechanics were used to calculate the thermodynamic correction including zero-point-energy (ZPE), thermal energy and entropy derived from partition functions.<sup>63,64</sup> (see SI-1 for details).

As we mentioned in the introduction, SAPO-34 is a specific type of silicoaluminophos-



phate zeolite with chabazite (CHA) structure;<sup>65</sup> the composition of unit cell is  $H_xSi_xAl_6P_{6-x}O_{24}$ . Experimentally, the of Si in SAPO-34 ( $Si/(Si+Al+P)$ ) is usually larger than 0.1,<sup>66,67</sup> and the value of  $x$  can be up to 1.32 as a result of magic-angle spinning NMR analysis.<sup>68,69</sup> In this work, we built a Cu-SAPO-34 ( $1 \times 1 \times 2$ ) supercell with a  $x$  value of 1.5 to represent the zeolite. Two H atoms were removed from the supercell to compensate the positive charge of the introduced  $Cu^{2+}$  ion, and the final chemical formula of the supercell is  $CuHSi_3Al_{12}P_9O_{48}$ . Similar models have been employed by Termath *et al.*<sup>70</sup> and Uzunova *et al.*<sup>68,71,72</sup> This model is reasonable for investigating the  $NH_3$ -SCR process since both Brønsted acid (H) and Lewis acid (Cu) are included in the supercell. During the calculations, the Brillouin zone was sampled at the gamma point, which is appropriate for this insulator.<sup>12</sup> The adsorption energy ( $\Delta G_{ad}$ ) was defined as:

$$\Delta G_{ad} = G_{adsorbate+zeolite} - G_{adsorbate} - G_{zeolite} \quad (3)$$

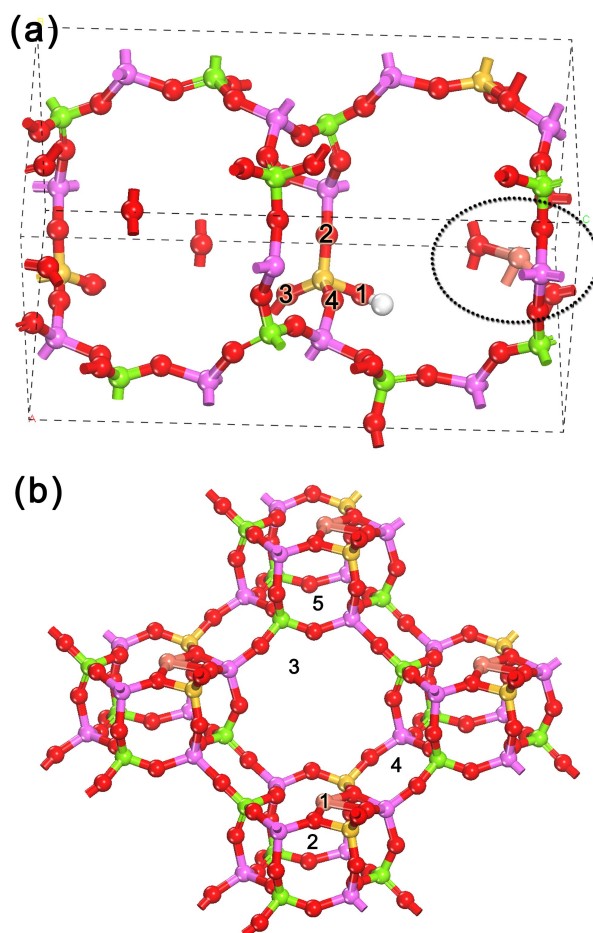
where  $G_{zeolite}$ ,  $G_{adsorbate}$ , and  $G_{adsorbate+zeolite}$  are the free energies of the zeolite, adsorbate in the gas phase, and adsorbate adsorbed on the zeolite, respectively.

## 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 Cu loading content, as mentioned in the introduction, Cu was suggested to locate slightly above the six-membered ring near two Si atoms (position 1 in Fig. 1b)<sup>2,14</sup> as a divalent ion ( $Cu^{2+}$ ). To validate this view, we examined the energies of Cu-SAPO-34 with  $Cu^{2+}$  in different positions (1–5 in Fig. 1b) and ensured that position 1 is the most stable one (Tab. S1 in SI). We can see from the figure that Cu is coordinated with four O atoms in the six-membered ring with distances of 2.08, 1.95, 1.91, and 2.36 Å, which are quite similar to the results of Uzunova *et al.*<sup>68,71,72</sup>

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4 There are two Si atoms in the ring, while the remaining Si is accompanied by a H atom to  
5 form a Brønsted acid site. The stabilities of different H positions (1–4 in Fig. 1a) were also  
6 tested. Positions 1–4 show very close stabilities, among which position 1 is slightly preferable  
7 (Tab. S2 in SI). The volume of the relaxed supercell was calculated to be  $1662.5 \text{ \AA}^3$ , very  
8 close to the experimental value ( $1644.8 \text{ \AA}^3$ ).<sup>69,73</sup>  
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Figure 1: 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.

In reaction equations (1) and (2), the reactants of SCR are  $\text{NH}_3$ ,  $\text{NO}$ ,  $\text{O}_2$ , and  $\text{NO}_2$ . We subsequently investigated the adsorption of these species and water on both Brønsted acid (B-site) and Lewis acid (L-site) sites, the best adsorption structures of which are illustrated in Fig. 2. In the figure,  $\text{H}_2\text{O}$  exhibit moderate adsorption on B- and L-sites, while both  $\text{NO}_2$

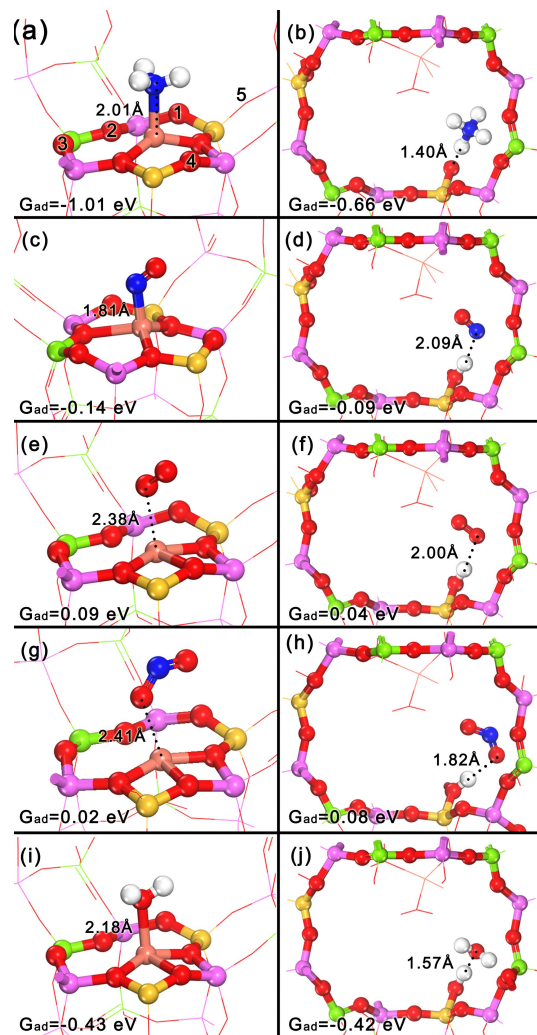


Figure 2: Structural illustration of the adsorption of NH<sub>3</sub> (ab), NO (cd), O<sub>2</sub> (ef), NO<sub>2</sub> (gh), and H<sub>2</sub>O (ij). The left and right columns refer to the Lewis acid (Cu<sup>2+</sup>) and Brønsted acid (H) site, respectively.

and O<sub>2</sub> hardly adsorb on the zeolite. NO prefers to slightly bond with the Cu<sup>2+</sup> ion by its N end. NH<sub>3</sub> binds strongly on both sites, and it will exist as NH<sub>4</sub><sup>+</sup> on B-sites. The results indicate that L-sites will be dominantly covered by NH<sub>3</sub> and a small amount of NO at the start of SCR process, and the B-site by NH<sub>3</sub>. It is in accordance with the generally accepted opinion that NH<sub>3</sub> and NO shall react on L-sites whereas B-sites serve as a NH<sub>3</sub> reservoir in the beginning of the reaction.<sup>4,74</sup> The NH<sub>3</sub> on B-sites could migrate to L-sites as the reaction proceeds.

## Formation of the N–N bond

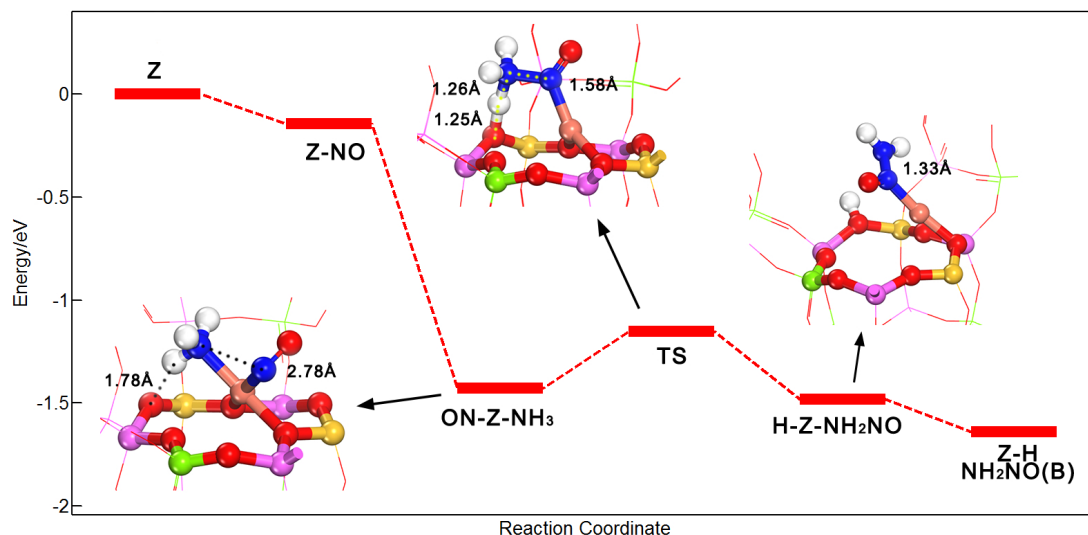
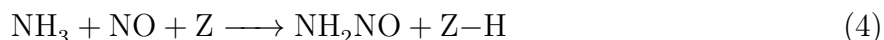


Figure 3: Free energy profile of the N–N coupling process. Some key structures are illustrated as inserts. (B) in the  $\text{NH}_2\text{NO}$  (B) indicates that it has been transferred to a Brønsted acid site.

The full mechanism of  $\text{NH}_3$ -SCR is considerably complicated.<sup>3,10</sup> Among that, N–N coupling is a crucial step towards the formation of nitrogen; therefore, it will be investigated first in this paper. Considering the valence of N in  $\text{N}_2$  (0), the coupling of two N atoms shall come from  $\text{NH}_3$  (-3) and NO (+2), respectively. According to this principle, we tried numerous possible reaction schemes of NO with  $\text{NH}_3$  in order to form N–N bond, but all of them failed: a huge repulsion would occur when N in NO approaches  $\text{NH}_3$ ; the NO would be pushed away if they are forced to be close. This is reasonable since N in  $\text{NH}_3$  is saturated (Fig. 2a); therefore, the possibility of direct attacking of NO to  $\text{NH}_3$  is ruled out. Then, in order to circumvent the problem of saturated  $\text{NH}_3$ , we tried to remove one H from the  $\text{NH}_3$  to form  $\text{NH}_2$  because  $\text{NH}_2$  is unsaturated, which would be easier for NO to react. Five positions indicated in Fig. 2a were considered to locate H after  $\text{NH}_3$  decomposition. However, from the results in Fig. S1, we found that all these pathways are extremely unfavourable thermodynamically; their free energies are 0.94 ~ 1.98 eV higher than that in Fig. 2a, let alone kinetic barriers. So, it would be very difficult to directly remove one H from  $\text{NH}_3$ .

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3 Since both of above reaction schemes are very difficult to occur over zeolites, we considered  
4 if other species in SCR reaction could facilitate the process. After numerous attempts and  
5 calculations, we found that with the assistance of NO, the N-H bond breaking would be  
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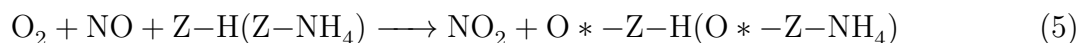


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12 where Z indicates the zeolite. We subsequently investigated relevant intermediates and tran-  
13 sition states of the reaction, whose structures and energies are displayed in Fig. 3. It proves  
14 that with NO, the reaction barrier would be much lower compared with dehydrogenation of  
15 NH<sub>3</sub> alone. In Fig. 3, NO and NH<sub>3</sub> would adsorb on the Cu<sup>2+</sup> with considerable free energy  
16 declines (1.43 eV). It is worth noting that in the insert (ON-Z-NH<sub>3</sub>) of Fig. 3, one H in the  
17 NH<sub>3</sub> is quite close to a framework O (1.78 Å), indicating a hydrogen bond interaction be-  
18 tween them. Then, in the transition state, NH<sub>3</sub> would approach the framework O, intending  
19 to bond it with the H. The distance between two N atoms, at the same time, is shortened  
20 (1.58 Å). Finally, since the bonding of two N would release a large amount of energy com-  
21 pensating the energy needed to break the N-H bond in NH<sub>3</sub>, two N atoms couple to form  
22 NH<sub>2</sub>NO while the H remains on the framework O (insert H-Z-NH<sub>2</sub>NO in Fig. 3). The energy  
23 barrier for this process was calculated to be 0.28 eV, an exceptionally small value, indicating  
24 that reaction 4 is a very effective way to activate the NO in NH<sub>3</sub>-SCR. We further made a  
25 frequency analysis to ensure its accuracy. The results showed that the transition state here  
26 exhibited one and only one imaginary frequency, which corresponds to N-N coupling and  
27 N-H breaking with a value of 450.5i cm<sup>-1</sup>. The NH<sub>2</sub>NO would transfer to B-sites for further  
28 decomposition, which will be demonstrated in the last subsection. In addition, we made a  
29 Bader analysis on Cu ion before (Z) and after (Z-H) N-N coupling reaction, finding that the  
30 valence of Cu ion changes from 1.12 to 0.69 which means that Cu<sup>2+</sup> is partly reduced to Cu<sup>+</sup>.  
31 The result is quite reasonable, since we can see from the left column of Fig. 2 and schemes  
32 in Fig. 3 that before N-N coupling, Cu<sup>2+</sup> ion tend to coordinate with four atoms, while the  
33 coordination number of Cu<sup>+</sup>, after the reaction, becomes two (scheme H-Z-NH<sub>2</sub>NO in Fig.  
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3). The results agree well with the general principle in coordination chemistry. Deep insight into the valence change of Cu ion and the intrinsic reason why the reaction can happen over zeolites by such a low-energy-barrier mechanism will be presented in the discussion section.

## NO and Cu<sup>+</sup> oxidation by O<sub>2</sub>

Although the whole reaction is the reduction of NO<sub>x</sub>, O<sub>2</sub> plays a crucial role in the SCR process.<sup>4,10</sup> Some researchers argued that in standard SCR O<sub>2</sub> will oxidise NO into NO<sub>2</sub>, resulting a fast SCR; however, other studies argued that standard and fast SCR may exhibit distinct mechanisms.<sup>50,75</sup> Currently, a clear mechanism for NO oxidation to NO<sub>2</sub> on the Cu ion is under debate and have not been achieved yet. Some previous studies stated that NO was oxidised by O<sub>2</sub> in the gas phase or in pores of zeolites (O<sub>2</sub> + 2NO → 2NO<sub>2</sub>),<sup>36</sup> but it is a three-molecule reaction thus its contribution to the overall NO oxidation is limited. We suggest that the elementary reaction is



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), and O\* indicates an adsorbed O atom over the Cu ion. It should be noted that NH<sub>3</sub> can readily adsorb on this H site ( $G_{ad} = -1.19$  eV), forming NH<sub>4</sub><sup>+</sup> on the ring (Z-NH<sub>4</sub>, Fig. S2b). Then, we investigated the adsorption of O<sub>2</sub> on Cu ion site as well as the energy barriers and free energy change of above reaction, the energy diagrams of which are shown in Fig. 4.

From the results, we can notice that the adsorption energy of O<sub>2</sub> increases significantly after Cu<sup>2+</sup> being reduced to Cu<sup>+</sup> with a H on the six-membered ring ( $G_{ad}$  from 0.52 eV to ~ 0 eV). Then, effective energy barriers on Cu<sup>+</sup> site (Z-H 1.06 eV and Z-NH<sub>4</sub> 0.86 eV) is found to be much lower than that on Cu<sup>2+</sup> (3.65 eV). This agree well with the previous work that Cu<sup>2+</sup> ions are incapable of activating O<sub>2</sub>,<sup>76</sup> and Cu<sup>+</sup> plays role of catalysing NO

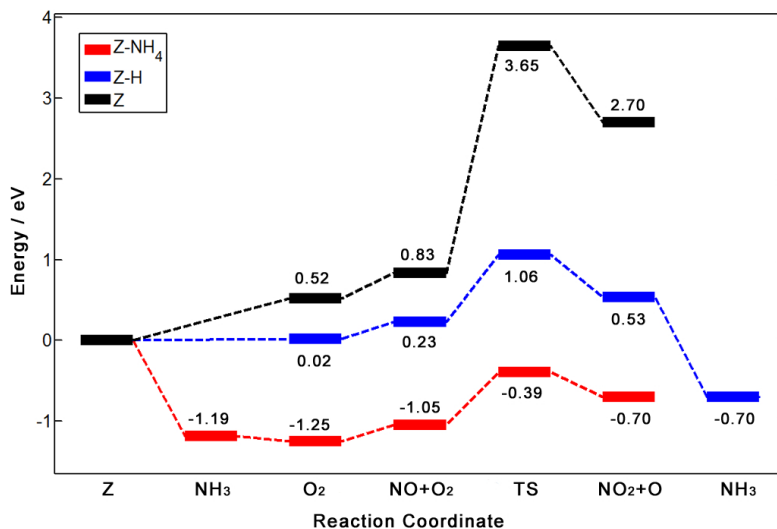


Figure 4: Free energy diagrams of  $O_2$  oxidation on zeolite (Z, black), Z-H (blue), and Z- $NH_4$  (red). For Z and Z-H pathway,  $O_2$  and NO will adsorb on Cu site and react to yield  $NO_2$  and O through the transition state,  $NH_3$  will adsorb on Z-H after that (corresponding to structures in Fig. S2(a, c) and Fig 5(b, d, f)); for Z- $NH_4$  pathway, one  $NH_3$  would adsorb first, then followed by  $O_2$ , NO adsorption and the transition state (corresponding to structures in Fig. S2(b, d) and Fig. S3(b, d, f))

oxidation.<sup>11</sup> We also considered the attacking of NO to  $O_2$  from gas phase (Fig. S3(a, c, e) and Fig. 5(a, c, e)), the energy barriers of which are over 1 eV, unfavourable compared with NO and  $O_2$  co-adsorbing on Cu site. After that, the produced  $NO_2$  can react with its neighbouring  $NH_4^+$  (Fig. S3f or Fig. 5f with  $NH_3$  adsorption) to form  $NH_4NO_2$ , leaving an O atom over the zeolite. The left O atom is very active and can readily react with NO to form  $NO_2$  with a considerable energy decline of 2.67 eV. Therefore, the NO oxidation reaction over Cu-SAPO-34 zeolites can be expressed as follows:



It is well recognized that  $NH_4NO_2$  is easy to stoichiometrically decompose into  $N_2$  and  $H_2O$  under SCR operation condition:<sup>2,4,10,15</sup>



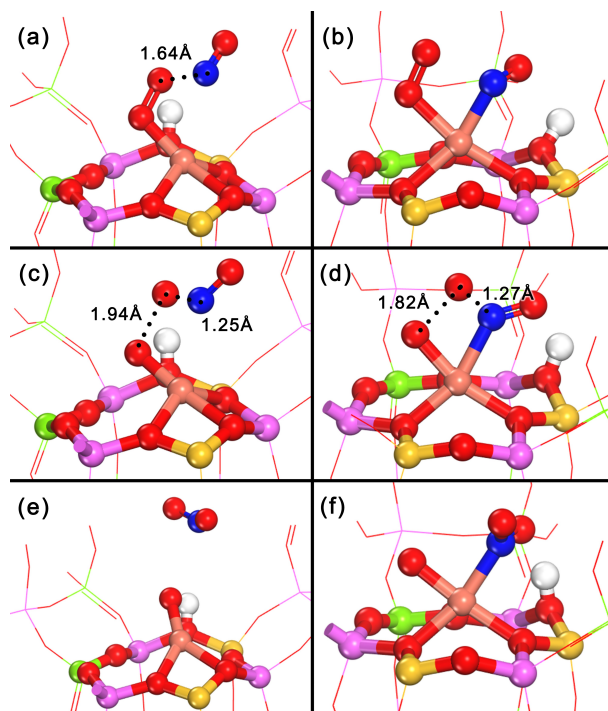


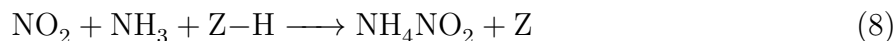
Figure 5: Structural illustration of NO oxidation on the reduced Cu ion site (Z-H). (a, b), (c, d), and (e, f) correspond to the initial, transition, and final states, respectively. In the left column, NO attacks from the gas phase while NO and O<sub>2</sub> co-adsorbed in the right.

To sum up, reaction 4 and 5 not only couple the N–N bond and form NH<sub>2</sub>NO and NH<sub>4</sub>NO<sub>2</sub>, 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<sub>3</sub> and NO is 1:1, while the oxidation states of N in them is a mismatch (-3 in NH<sub>3</sub> and +2 in NO). Therefore, the coupling of N–N bond in NH<sub>3</sub> and NO must be accompanied by the reduction of L-site (Cu<sup>2+</sup> → Cu<sup>+</sup>) which will be regenerated by the oxidation of O<sub>2</sub>. The redox cycle explains well the experimental observation that steady state NO conversion would decrease to zero after O<sub>2</sub> cut-off under standard SCR conditions.<sup>28</sup> According to their study, the content of Cu<sup>+</sup> increases to 75–95% of the whole Cu species, and SCR reactions would be soon stopped since N–N coupling cannot happen on Cu<sup>+</sup> site.

If we consider fast SCR (reaction 2) with NO<sub>2</sub> involved, NO oxidation is not necessary



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3 after N–N coupling and the reaction goes as follows:  
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11  $\text{NO}_2$  and  $\text{NH}_3$  can strongly adsorb on  $\text{Cu}^+$  and framework H ( $G_{ad} = -0.86$  and  $-1.19$  eV  
12 in Fig. S2e and S2b, respectively), and  $\text{NO}_2$  can naturally attack its neighbouring  $\text{NH}_4^+$  to  
13 form  $\text{NH}_4\text{NO}_2$  (Fig. S2f).<sup>28</sup>  
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17 After N–N coupling (equation 4) and NO oxidation (equation 6), the copper restores to  
18  $\text{Cu}^{2+}$  and the remaining reactants for standard SCR are one NO,  $\text{NO}_2$  and two  $\text{NH}_3$ . Inter-  
19 estingly, these are exactly the reactants of fast SCR (reaction 2), which would be complete  
20 through reaction 4, 8, and 7. It should be noted that we also tried another mechanism after  
21 NO oxidation, which is shown in supporting information 5.  
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## 28 **$\text{NH}_2\text{NO}$ decomposition into $\text{H}_2\text{O}$ and $\text{N}_2$**

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32 The  $\text{NH}_2\text{NO}$  formed in above stages will decompose into  $\text{H}_2\text{O}$  and  $\text{N}_2$  to complete the whole  
33 SCR process. Previous studies showed that it is a relatively easy process on the B-site of  
34 zeolites by a hydrogen push-pull mechanism.<sup>35,36</sup> We investigated its decomposition on both  
35 Brønsted acid and Lewis acid sites, and all intermediates and transition states were identified  
36 (Fig. S5). It can be seen from the scheme in Fig. 6 that the configuration of  $\text{NH}_2\text{NO}$  will  
37 change several times by the transferring of H atom, which was well recognised by previous  
38 studies.<sup>36,77</sup> We firstly tried this process on the L-site (Fig. S5), but the energy barrier of the  
39 first step of  $\text{NH}_2\text{NO}$  decomposition in L-acid, the proton transferring from N to O, was very  
40 high (2.03 eV). From Fig. S5b, we can see that during the intra-molecular proton transfer,  
41 an unstable four-membered ring is formed, exerting a strong steric hindrance and making  
42 L-side unfavourable for catalysing this reaction. On the other hand, energy barriers of the  
43 reactions on the B-site are moderate, making it easy to occur (the energy profile in Fig. 6,  
44 and corresponding structures in Fig. S6).  
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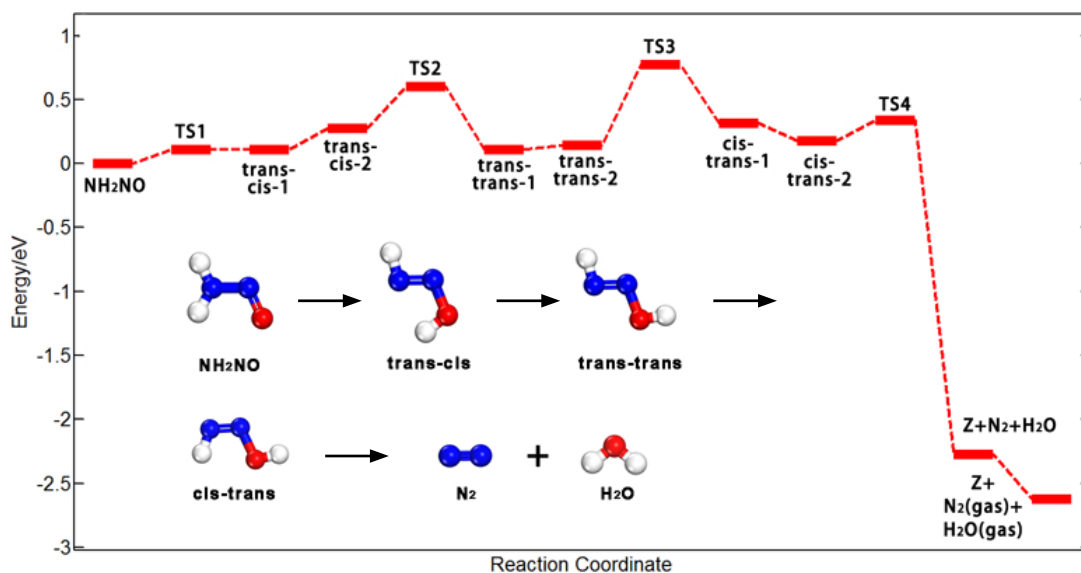
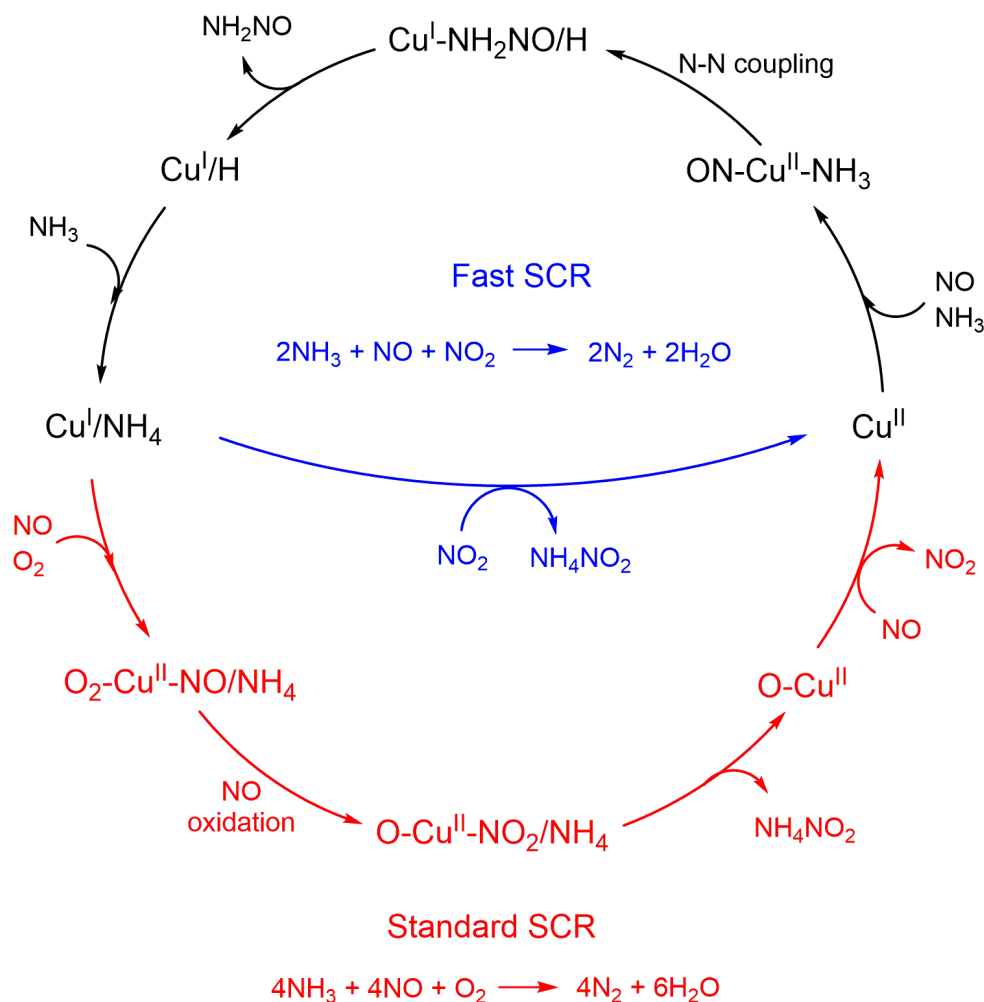


Figure 6: Total energy profile of  $\text{NH}_2\text{NO}$  decomposition on the B-site and a scheme of transformation of  $\text{NH}_2\text{NO}$ . Structures of intermediates and transition are displayed in Fig. S6.

As shown in Fig. S6a,  $\text{NH}_2\text{NO}$  adsorbs on the B-site by the interaction between O and H atoms, in which the B-site serves as a H reservoir, helping  $\text{NH}_2\text{NO}$  to transfer H by the so-called hydrogen push-pull mechanism. In the subsequent steps,  $\text{NH}_2\text{NO}$  transforms its configuration several times by donating and receiving H with the help of the framework and finally decomposes to  $\text{N}_2$  and  $\text{H}_2\text{O}$  with considerable energy release. The highest effective barrier<sup>63,78</sup> for the  $\text{NH}_2\text{NO}$  decomposition is 0.77 eV (from  $\text{NH}_2\text{NO}$  to TS3), which is much lower than that on the L-site. The results show that Brønsted acid and Lewis acid ( $\text{Cu}^{2+}$ ) sites would collectively catalyse  $\text{NH}_3$ -SCR over Cu-SAPO-34 zeolites.

## Overall mechanism

An overall picture of  $\text{NH}_3$ -SCR over Cu-SAPO-34 is schematically illustrated in Fig. 7. To the best of our knowledge, it is the first time that such a step-by-step reaction pathways of  $\text{NH}_3$ -SCR over Cu-SAPO-34 is presented from periodic DFT calculations. For the standard SCR, the reaction is initialized by N–N coupling between NO and  $\text{NH}_3$  that co-adsorbed on the  $\text{Cu}^{2+}$  site to form  $\text{NH}_2\text{NO}$ ; then, NO is oxidised by  $\text{O}_2$ , which further react with



37 Figure 7: Schematic illustration of the mechanism of fast and standard NH<sub>3</sub>-SCR over Cu-  
38 SAPO-34. It should be noted that NH<sub>4</sub>NO<sub>2</sub> and NH<sub>2</sub>NO will decompose to N<sub>2</sub> and H<sub>2</sub>O  
39 stoichiometrically (equation 7 and scheme in Fig. 6), and it is not showed in the figure for  
40 clarity.

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43 NH<sub>3</sub> to produce NH<sub>4</sub>NO<sub>2</sub>, leaving on O atom on the Cu site. After that, the O atom will  
44 further oxidise NO to yield NO<sub>2</sub>. Next, the active site is restored to pure Cu<sup>2+</sup> and react  
45 with remaining two NH<sub>3</sub>, one NO and NO<sub>2</sub> to form one NH<sub>4</sub>NO<sub>2</sub> and NH<sub>2</sub>NO. Finally,  
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47 NH<sub>4</sub>NO<sub>2</sub> and NH<sub>2</sub>NO decompose into N<sub>2</sub> and H<sub>2</sub>O. Among all these process, the effective  
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49 free energy barrier of NO oxidation is the highest (0.86 eV) and may thus be regarded as the  
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51 rate-limiting step.  
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55 From the mechanism, we can notice that the standard SCR has to go through both NO  
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57 activation (coupling with NH<sub>3</sub>) and NO oxidation processes, which are closely related with  
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4 each other to ensure the whole reactions to be completed. Firstly, NO and NH<sub>3</sub> will couple  
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6 with the assistance of O in the framework to produce NH<sub>2</sub>NO and reduce Cu<sup>2+</sup> to Cu<sup>+</sup>.  
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8 Then, NO will be oxidised over Cu<sup>+</sup> site to further form NH<sub>4</sub>NO<sub>2</sub>; however, in addition to  
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10 producing NO<sub>2</sub>, a more vital role of NO oxidation is to regenerate Cu<sup>2+</sup> site to keep reactions  
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12 on going. Without it, the zeolite will be soon saturated with reduced Cu<sup>+</sup> species, and the  
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14 overall reaction will be stopped. With these two essential processes, the standard SCR can  
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16 proceed continuously, producing N<sub>2</sub> by the stoichiometric decomposition of NH<sub>4</sub>NO<sub>2</sub> and  
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18 NH<sub>2</sub>NO.

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20 Comparing with Cu-SSZ-13, which is currently in commercial use and attracted most  
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22 attentions in the past decades, our work represents one of few DFT studies on NH<sub>3</sub>-SCR  
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24 mechanism over Cu-SAPO-34, well extending beyond what have been published on SSZ-13.  
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26 The location of active Cu site, the redox cycle of Cu<sup>+</sup> and Cu<sup>2+</sup>, and the coupling of N–N  
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28 bond are quite similar on these two zeolites. Both NH<sub>3</sub> and NO are required for N–N coupling  
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30 and Cu<sup>2+</sup> would be reduced to Cu<sup>+</sup> to complete the reduction of the redox cycle, which is  
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32 in agreement with experiments.<sup>11,28</sup> Some notable differences, on the other hand, appear  
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34 on the NH<sub>2</sub>NO decomposition and NO oxidation. Previous literatures suggested that the  
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36 effect of Brønsted acid sites are rather limited.<sup>11,25,37</sup> It is found that the SCR activity under  
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38 473 K is not dependent on the amount of Brønsted acid sites. Based on this experimental  
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40 observation, the Brønsted acid site may not be a part of SCR process, and thus it can only  
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42 influence SCR activity by altering the acidity of zeolite or interacting with neighbouring Cu  
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44 site. Gao *et al.*<sup>17</sup> pointed out that Brønsted acidity favors the standard NH<sub>3</sub>-SCR without  
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46 being an essential ingredient of the active site. However, according to our results, Brønsted  
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48 acid sites are necessary for NH<sub>2</sub>NO decomposition which is difficult to occur on Cu sites.  
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50 Through a hydrogen push-pull mechanism, we showed that Brønsted acid sites could readily  
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52 catalyse the decomposition of NH<sub>2</sub>NO, also in agreement with some theoretical studies.<sup>6,35,36</sup>  
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54 The fact that the SCR activity does not depend on the Brønsted acid can be reconciled by  
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56 realizing that there are usually more Brønsted acid sites than Lewis acid sites in zeolites;  
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3 only a small portion of Brønsted acid sites would take part in the SCR while Lewis acid  
4 sites are saturated with the reaction. Therefore, the amount of Brønsted acid sites would  
5 not significantly influence the SCR activity.  
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10 The pathway of NO oxidation we presented in this contribution is also different from  
11 the literature works. Janssens *et al.*<sup>11</sup> suggested that NO and O<sub>2</sub> would react on the Cu<sup>+</sup>  
12 site to form Cu<sup>2+</sup>NO<sub>3</sub><sup>-</sup>, followed by the oxidation with another NO to produce NO<sub>2</sub> and  
13 Cu<sup>2+</sup>NO<sub>2</sub><sup>-</sup>. Our mechanism, on the other hand, do not include NO<sub>3</sub><sup>-</sup> species in the NO  
14 oxidation since our DFT calculations showed that the free energy of Cu<sup>2+</sup>NO<sub>3</sub><sup>-</sup> is rather  
15 high. However, both Janssens *et al.* and we agree that NO oxidation is the rate-limiting  
16 step, and all the elementary steps involved in the fast SCR are also parts of the standard  
17 SCR. It seems contradictory to the work of Tronconi *et al.*,<sup>50,75</sup> who observed that the rate  
18 of NO oxidation is much slower than SCR process. This puzzle can be understood from Fig.  
19 7. We can see that the NO oxidation in SCR is part of the reaction cycle rather than a  
20 isolated step; the NO oxidation alone would be slow in zeolite since most Cu site in zeolites  
21 are Cu<sup>2+</sup> without the SCR redox cycle, while NO oxidation is favoured only when the site  
22 is reduced to Cu<sup>+</sup>.<sup>11</sup>  
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## 38 General discussion of the zeolite chemistry

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40 In the last several decades, zeolites have been widely used in the fields of petrochemical  
41 industry, fine chemicals, and other heterogeneous reactions.<sup>79-82</sup> As crystalline microporous  
42 materials, zeolites own many novel properties, such as species migration, ion exchange, and  
43 adsorption, which give us more efficient and cheap alternatives for some traditional catalytic  
44 reactions. The relation between the structure of Cu-SAPO-34 zeolites and activities of SCR  
45 process, however, has not been well understood. We therefore make a general discussion  
46 about its structure-activity relationship in this subsection, aiming to supplement current  
47 understandings on zeolite chemistry in general.  
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57 Starting from an isolated Cu<sup>2+</sup> ion, the first step of SCR is the N-N coupling between  
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4 NO and NH<sub>3</sub> that goes through a small barrier (0.28 eV). One question naturally arises here:  
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6 why can NO be activated with such a low energy barrier? The origin lies in the special  
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8 zeolite structure: in Cu-SAPO-34, the diameter of the six-membered ring is about 5 ~ 6  
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10 Å, and the structure of transition state (Fig. 3) fits such a ring well for the N–N coupling;  
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12 the whole molecule (NH<sub>2</sub>NO) bridges from the Cu ion to a O in the framework with a quite  
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14 reasonable structure. One of H in the NH<sub>3</sub> will interact with this O by the hydrogen bond,  
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16 thus lowering the energy of the transition state. Meanwhile, the six-membered ring will  
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18 also stretch to some extent to fit the structure of transition states owing to the flexibility of  
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20 zeolite framework. Moreover, the weakened N–H bond of the transition state also provides  
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22 its N more space to couple with another N. These features of zeolites may partly explain  
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24 their good performance on NH<sub>3</sub>-SCR. Therefore, it was reasonable that the N–N coupling  
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26 process over Cu-SSZ-13 goes through a similar pathway since the geometrical structures of  
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28 SAPO-34 and SSZ-13 are similar.

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30 Equally important, deep insight into the redox cycle in zeolites has been achieved in this  
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32 work. From Fig. 7, we can notice that the valence of Cu ion in Cu–NH<sub>2</sub>NO/H, Cu/H, and  
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34 Cu/NH<sub>4</sub> are +1 while for the rest species it is +2 (measured by the Bader charge analysis,  
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36 details in Tab. S3). The redox cycle is very important in the whole SCR process especially  
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38 for the standard SCR, since Cu<sup>2+</sup> is not able to activate O<sub>2</sub> molecules and the involvement of  
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40 Cu<sup>+</sup> is crucial for NO oxidation according to the results in the last section. Aiming to clarify  
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42 the role of zeolites in such a redox cycle, we calculated the valence number of each atom in  
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44 the six-membered ring of Cu<sup>2+</sup> and Cu<sup>+</sup> (Fig. 8ab). In Fig. 8b, one H remains on the O  
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46 in the framework after the N–N coupling, and most of its electron will transfer to the Cu  
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48 through the framework, which eventually reduces Cu<sup>2+</sup> into Cu<sup>+</sup>. Moreover, isosurfaces of  
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50 charge density difference before and after O<sub>2</sub> adsorption on these two Cu sites are presented  
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52 in Fig. 8cd. It is clear from Fig. 8c that the bonding between O<sub>2</sub> molecule and Cu<sup>2+</sup> is very  
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54 limited, because it is difficult for Cu<sup>2+</sup> to donate electrons to O<sub>2</sub>, because it is on the highest  
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56 oxidation state. On the other hand, we can see from Fig. 8d that ceCu+ has a considerable  
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interaction with  $O_2$  by electron accumulation on  $O_2$  and depletion on  $Cu^+$ . According to the Bader charge analysis, the valence of Cu and two O atoms before and after adsorption are 0.69, 0, 0, and 1.01, -0.25, -0.1, respectively, indicating that 0.35 electrons are donated from Cu ion and the framework to  $O_2$ , and  $Cu^+$  partly resumes to  $Cu^{2+}$ . Therefore, the O–O bond in the  $O_2$  molecule is activated upon adsorption on  $Cu^+$ , leading to a stronger  $O_2$  adsorption energy and lower energy barrier for NO oxidation.

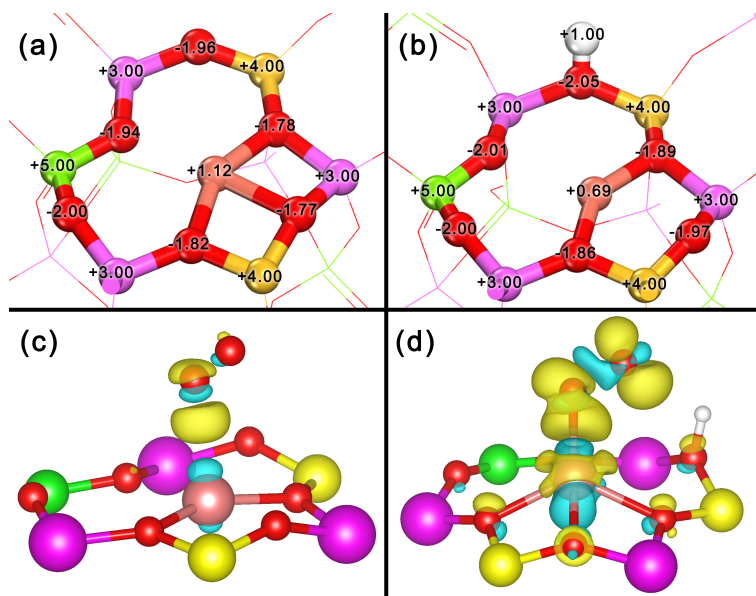


Figure 8: Bader charge of the six-membered ring loaded with  $Cu^{2+}$  (a) and  $Cu^+$  (b); isosurfaces (level: 0.0025) of charge density difference before and after  $O_2$  adsorption on  $Cu^{2+}$  (c) and  $Cu^+$  (d). Yellow indicates the electronic accumulation and light blue for depletion.

In addition to the Lewis acid site (Cu ion), the last part of SCR process, the decomposition of  $NH_2NO$ , occurs on the Brønsted acid site with moderate energy barriers. Our calculations show that the adsorption free energy of  $NH_2NO$  on the Cu site is close to zero; therefore, it could readily transfer to Brønsted acid sites in the cage.  $NH_2NO$  is difficult to decompose on the Lewis acid sites due to a large intra-molecular proton transfer barrier, while the Brønsted acid sites can facilitate this process by a hydrogen push-pull mechanism. It means that Brønsted acid and Lewis acid sites collectively catalyse the reaction, and such a "multi-site" concept of catalysis is receiving increasingly attention in recent years.<sup>64,83</sup>

Finally, both similarities and differences can be found comparing the SCR activity on

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3 traditional metal oxide catalysts with zeolites. In metal oxides (*e.g.* MnO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>), it  
4 is possible for NH<sub>3</sub> to donate one H to surface O with a reasonable barrier,<sup>84,85</sup> but such  
5 a pathway is not practical on zeolites since the ability of zeolite framework to accept H is  
6 inferior to that of oxides. On CHA-type zeolites, the six-membered ring serves as a bridge  
7 to facilitate the coupling of N–N bond as well as the breaking of N–H bond in NH<sub>3</sub>. On the  
8 other hand, there is a similar concept of redox cycle of active site and interplay between the  
9 Brønsted acid and Lewis acid sites on traditional catalysts. Taking V<sub>2</sub>O<sub>5</sub> as an example,  
10 V<sup>5+</sup>, which serves as Lewis acid site, will be reduced to V<sup>4+</sup> when NO react NH<sub>3</sub> to produce  
11 N<sub>2</sub> and H<sub>2</sub>O; it then resumes to V<sup>5+</sup> during NO oxidation. The Brønsted acid site (H) over  
12 metal oxides can also facilitate NH<sub>2</sub>NO decomposition process.  
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## 26 Conclusion

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29 In this work, a comprehensive investigation of NH<sub>3</sub>-SCR process over Cu-SAPO-34 zeolites  
30 was carried out by virtue of periodic DFT calculations using hybrid functional. Van der  
31 Waals (vdW) interactions were also considered throughout the calculation, the main conclu-  
32 sions of which are the following:  
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- 37 (i) A detailed step-by-step NH<sub>3</sub>-SCR mechanism over Cu-SAPO-34 was obtained with  
38 moderate energy barriers and reasonable intermediate structures.  
39
- 40 (ii) A NO-assisted N–H bond breaking mechanism of NH<sub>3</sub> was determined to account for  
41 the N–N formation between NO and NH<sub>3</sub>. The NO is activated by binding with N  
42 in NH<sub>3</sub> to form NH<sub>2</sub>NO while one of its N–H bond is weakened. The extra H would  
43 remain at the six-membered ring of the zeolite, reducing the original Cu<sup>2+</sup> into Cu<sup>+</sup>.  
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- 52 (iii) The NO oxidation by O<sub>2</sub> was shown to occur on reduced Cu site (Cu<sup>+</sup>), and the Cu<sup>+</sup>  
53 will resume to Cu<sup>2+</sup> after oxidation, completing the Cu<sup>2+</sup>/Cu<sup>+</sup> redox cycle.  
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- 58 (iv) A detailed decomposition mechanism of NH<sub>2</sub>NO in the Brønsted acid site was iden-  
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3 tified, confirming not only its feasibility, but also a collective efforts of Brønsted acid  
4 and Lewis acid ( $\text{Cu}^{2+}$ ) sites in catalysing  $\text{NH}_3$ -SCR over Cu-SAPO-34 zeolites.  
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8 The relation of above conclusions to the structural and electronic properties of zeolites,  
9 including their special six-membered ring structure, influence of the framework H on the  
10 valence of loaded metal ion, collective efforts by Brønsted acid and Lewis acid sites, are  
11 discussed and compared with previous literatures. These features may be extended to other  
12 catalytic reactions over zeolites and would supplement current understandings on not only  
13 SCR over Cu-CHA but also on general zeolite chemistry.  
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## 47 Supporting Information Available

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50 Details of additional notes, structures, and energies mentioned in the paper.

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52 This material is available free of charge via the Internet at <http://pubs.acs.org/>.  
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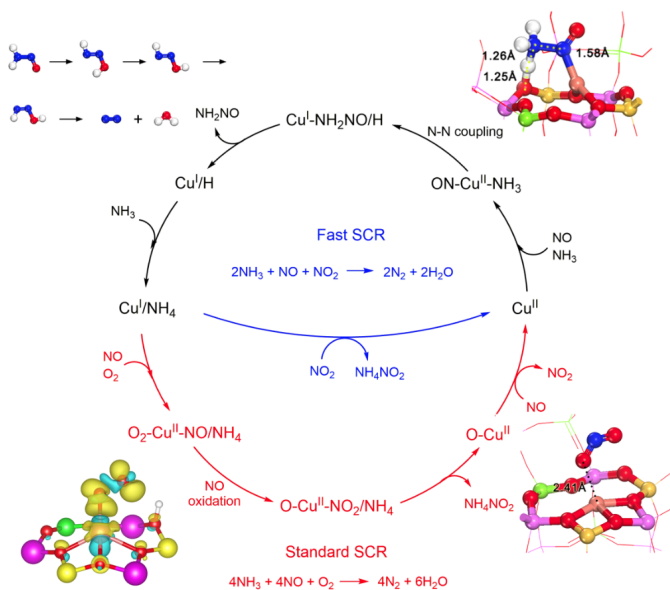
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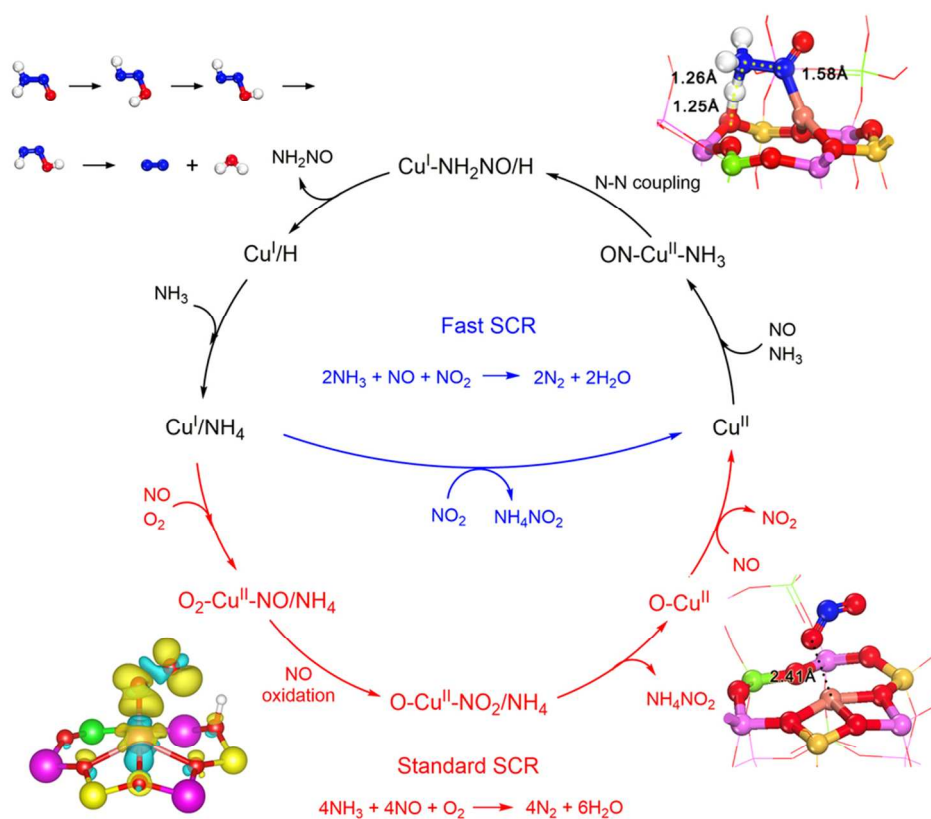
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## Graphical TOC Entry





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