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Quasi-operando quantification of Cu(II) ions in Cu-SSZ-13 catalyst by an NH_3 temperature-programmed reduction method

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A quasi-operando NH_3 temperature-programmed reduction method (NH_3-TPR), with N_2:Cu=1:1, is developed to quantify total Cu(II) ions in Cu-SSZ-13 quenched from SCR-relevant reactions, and its accuracy is confirmed by in-situ EPR. $[Cu(OH)]^+$-Z and Cu^{2+}-2Z can be further distinguished by NH_3 reduction temperatures, and their different reducibility in SCR is revealed.

Cu-SSZ-13 is a Cu-exchanged small-pore zeolite with chabazite (CHA) structure, which has shown outstanding activity and hydrothermal stability as a NO_x selective catalytic reduction (SCR) catalyst.[1, 2] During the past decade or so, tremendous efforts have been made for better understanding the fundamentals and applications of this catalyst. Under dehydrated conditions, this catalyst contains two isolated Cu(II) SCR active sites, *i.e.*, $[Cu(OH)]^+$-Z and Cu^{2+}-2Z (Z representing negatively charged framework $[Si\text{-}O\text{-}Al]^-$ group, illustrated by Fig. S1). In SCR reaction, both sites participate via a redox mechanism between Cu(II) and Cu(I) oxidation states.[3, 4] However, these Cu(II) sites may show different activities in low-temperature SCR, and their durability upon hydrothermal aging and sulfur poisoning is different.[5-7] Developing methodologies for quantifying various Cu sites is obviously important for establishing structure-activity relationships, and for the design of more active and robust catalysts. H_2 temperature-programmed reduction (H_2-TPR) is one of the most widely used methods for probing different Cu species in Cu-zeolites. However, Cu(II) ions are bonded to the zeolite framework under H_2-TPR operation but are typically coordinated by NH_3 and H_2O during low-temperature SCR,[8] so H_2-TPR cannot reveal the actual redox properties of Cu(II) ions under operando conditions.[9] Furthermore, quantification with H_2-TPR may be interfered by the presence of adsorbed species (*e.g.*, NH_3 and nitrates) that either act as reductants or consume H_2. These problems can be circumvented by running TPR using the reductive components of the SCR reactants (*e.g.*, NH_3 or NO+NH_3) as reductants. Recently, Villamaina et al.[9] reported a NO+NH_3-TPR method and found that Cu(II) ions can be quantified by the amount of N_2 formed during reduction. However, due to the strong reducibility of this mixture, reduction features of $[Cu(OH)]^+$-Z and Cu^{2+}-2Z cannot be readily distinguished. Alternatively, NH_3 alone can reduce Cu(II) to Cu(I) at temperatures higher than 100 °C.[10] Since NH_3 is a weaker reductant than NH_3+NO, NH_3-TPR may be capable of distinguishing the two Cu(II) sites. Note that Nanba et al.[11] have employed NH_3-TPR to identify two different active oxygen species in Ag/ZrO_2 catalysts that are otherwise hard to distinguish by H_2-TPR. Moreover, in contrast with H_2-TPR, Cu(II) ions under NH_3-TPR display similar Cu-NH_3 coordination as in SCR,[3] implying the prospect of NH_3-TPR to quantifying Cu(II) ions and comparing their redox properties in a quasi-operando manner.

Herein, we developed an NH_3-TPR method for quantifying Cu(II) ions in Cu-SSZ-13 catalysts pretreated under various conditions. Gaseous products from the interaction between Cu(II) species and NH_3 were quantified by an online mass spectrometer (MS, Pfeiffer Vacuum), and the changes in oxidation state of Cu were monitored by in-situ electron paramagnetic resonance (EPR, Bruker E580 X-band spectrometer, detailed instrument setup in Ref. 13). The stoichiometry of the reduction process was revealed for the first time, and the potential application of NH_3-TPR in studying the redox process of Cu during low-temperature SCR was illustrated.

A Cu-SSZ-13 catalyst with 1.34 wt.% Cu(II) content and Si/Al ratio of ~12 (detailed information provided in Supplementary Information) was used as an example to exhibit our typical NH_3-TPR procedure and result interpretation. After a pretreatment in 21% O_2/N_2 at 300 °C for 30 min and then purging in Ar at room temperature (to remove adsorbed O_2 on the catalyst, confirmed by Fig. S4), the catalyst (100 mg) was

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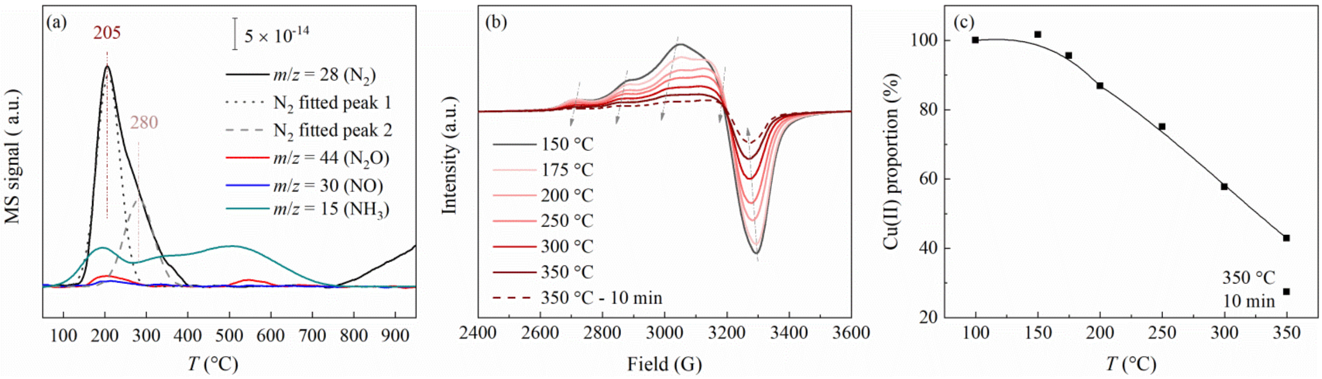

Fig. 1 (a) Gaseous products by MS, (b) in-situ EPR spectra and (c) EPR-derived Cu(II) proportion during NH_3-TPR of Cu-SSZ-13 with 1.34 wt.% Cu(II) content.

saturated in 1000 ppm NH_3/He (20 mL/min), and then the sample temperature was ramped to 1000 °C at a rate of 10 °C/min with continuous NH_3/He flow. N_2 (m/z = 28) is the dominant gaseous product from the reduction process, while only a little amount of N_2O (m/z = 44) is detected (contributing to less than 5% of total N-containing products) and NO (m/z = 30) amount is negligible (Fig. 1a). The high N_2/N_2O ratio of the gaseous products indicates the absence of CuO in our Cu-SSZ-13, as our control experiment using CuO-mixed SSZ-13 demonstrates large amount of N_2O formation (Fig. S5). The N_2 release feature between 100 and 400 °C appears asymmetric, which can be divided into two peaks via deconvolution, where the main peak at 205 °C and the shoulder feature at 280 °C have an area ratio of 0.63:0.37. On the basis of $[Cu(OH)]^+$-Z and Cu^{2+}-2Z quantification by H_2-TPR (0.64:0.36 in Fig. S3), we assign them to the reduction of (NH_3-solvated) $[Cu(OH)]^+$-Z and Cu^{2+}-2Z, respectively. N_2 release at temperatures higher than 700 °C originates mostly from NH_3 decomposition (Fig. S6). The reduction of Cu(II) by NH_3 was also monitored by in-situ EPR (Fig. 1b). Typical EPR features of Cu(II)-NH_3 complexes are readily observed when exposing the sample with NH_3 at 100 °C. With increasing temperature, both the hyperfine (2600-3200 G) and high-field (~3300 G) features shift towards lower fields, implying the transition from Cu(II)-NH_3 coordination partially to Cu(II)-O_f coordination (*e.g.*, transition from $[Cu(NH_3)_4]^{2+}$ to $[Cu(NH_3)_2(O_f)_2]^{2+}$, O_f represents framework oxygen atom) due to NH_3 desorption.[12] Since $[Cu(OH)]^+$-Z and Cu^{2+}-2Z are both EPR-active with NH_3 coordination,[13] total Cu(II) quantities can be obtained by double-integration of the EPR spectra. After calibrating the effect of temperature on EPR signal intensity,[14] the decrease of EPR-detectable Cu(II) proportion with increasing temperature (above ~150 °C) is clearly shown in Fig. 1c. Note that our EPR setup did not allow temperatures higher than 350 °C; instead, the sample was kept at 350 °C for 10 min in the presence of 1000 ppm NH_3, and some Cu(II) was still detected after this treatment. It should be mentioned that desolvation of NH_3-solvated $[Cu(OH)]^+$-Z would also contribute to a decrease in EPR signal intensity besides Cu(II) reduction, while Cu^{2+}-2Z is always EPR-detectable no matter whether it is solvated or not.[13] The finally measured Cu(II) proportion, ~25%, is lower than the initial proportion of Cu^{2+}-2Z (~37%), indicating that relatively stable Cu^{2+}-2Z is also reducible with NH_3, in accordance with the report of Godiksen et al.[14] The produced Cu(I) species, as a function of temperature, are anticipated to be $[Cu(NH_3)_2]^+$-Z, $[Cu(NH_3)O_f]^+$-Z or Cu^+-Z.[3, 10, 12]

The same NH_3-TPR tests were carried out on Cu-SSZ-13 catalysts with different Cu(II) contents (determined by H_2-TPR); a clear linear relationship between Cu(II) content and N_2 yield is obtained when Cu(II) content does not exceed 1.66 wt.% (Fig. 2). More importantly, the molar ratio between produced N_2 and reduced Cu is for the first time determined as ~1. This allows for possible mechanisms for Cu(II) reduction by NH_3, which have not been well established in literature, to be suggested here. It is inferred that Cu^{2+}-2Z reduction by NH_3 is initiated by heterolytic N-H bond breaking of the Cu(II)-NH_3 complexes, leading to the generation of Cu(I)-bonded amino (Cu^+-NH_2) intermediates and new Brønsted acidic protons, as shown by R1.[15] Even though this reaction has been computed to be difficult (activation energy ~120 kJ/mol),[16] study by Moreno-González et al.[12] suggests that the activation energy is lowered to ~30 kJ/mol with the assistant of solvation effects by NH_3 ligands (not written in NH_3-solvated forms in R1 for simplification, similarly hereinafter). The reduction of $[Cu(OH)]^+$-Z should be more facile as H_2O formation in this case provides a strong thermodynamic driving force (R2).[15] Upon formation of the Cu^+-NH_2 intermediates, they can combine with each other to form N_2H_4, and this latter species will then decompose to N_2 and H_2, as illustrated by R3.[10] However, a N_2/Cu molar ratio of 0.5 is predicted by such a reaction

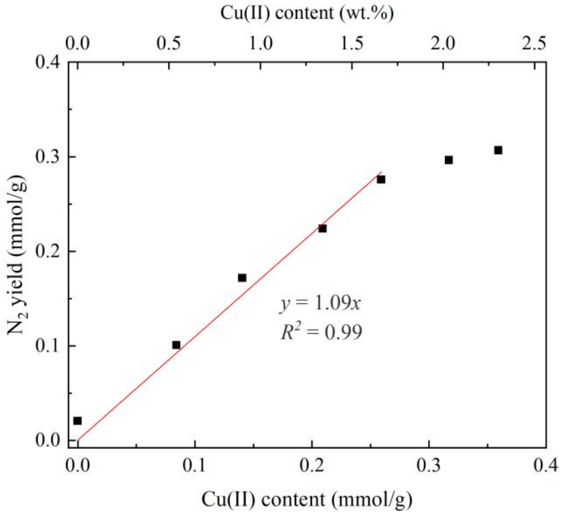

Fig. 2 Relationship between Cu(II) content and N_2 yield.

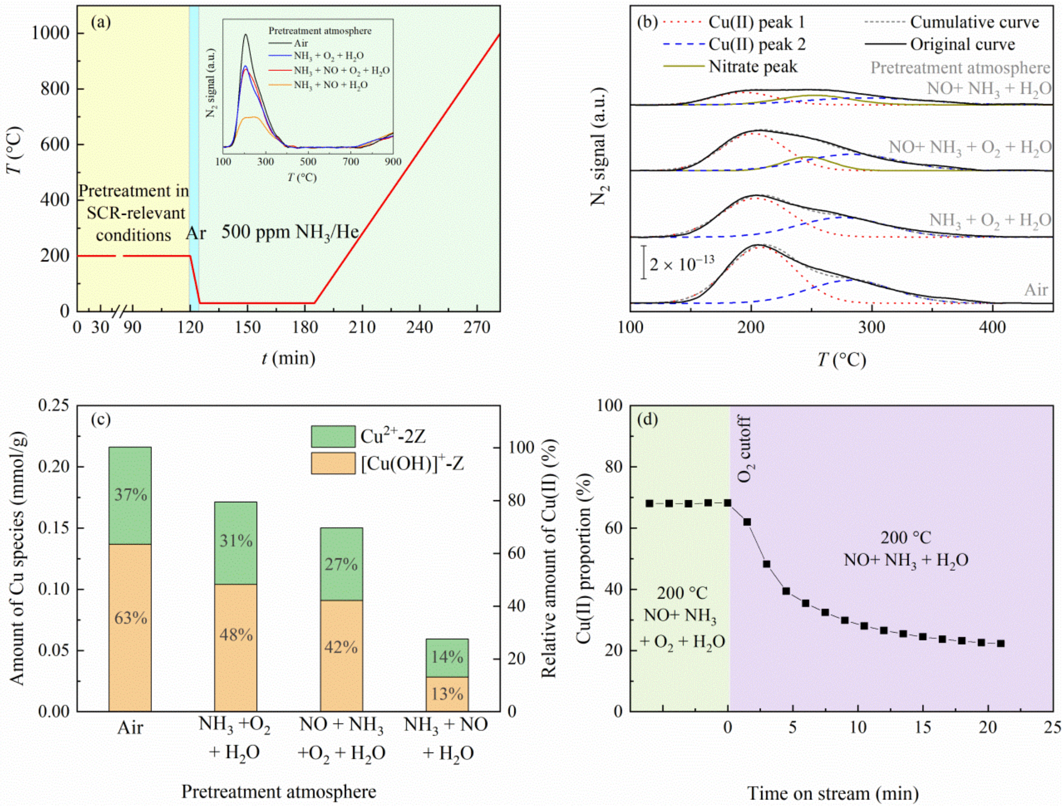

Fig. 3 (a) Scheme of test procedure (original N_2 release curves by MS shown in inset), (b) deconvolution of N_2 release curves, and Cu(II) proportion determined by (c) NH_3-TPR with MS and (d) in-situ EPR.

pathway, which cannot explain the observed 1:1 ratio. Alternatively, Cu^+-NH_2 may interact with NH_3 to produce N_2 (R4), which involves one N atom from Cu^+-NH_2 and the other from NH_3. The stoichiometric N_2/Cu ratio of 1 predicted by R4 indicates that this is a more plausible pathway for Cu^+-NH_2 conversion at relatively low Cu loadings (*i.e.*, ≤ 1.66 wt.% in Fig. 2), and the formation of H_2 is confirmed in Fig. S7, while R3 may be more pronounced with increasing Cu contents for N_2/Cu ratio lower than 1 (Fig. 2). By comparing the overall reduction reactions of Cu^{2+}-2Z (R5) and $[Cu(OH)]^+$-Z (R6), H_2O formation makes the latter reaction energetically more favorable and explains the lower reduction temperature of $[Cu(OH)]^+$-Z,[15] in accordance with calculations by Paolucci et al.[3] For further understanding the reduction mechanisms, more experimental and theoretical studies are required.

$$Cu^{2+} + NH_3 \rightarrow Cu^+ - NH_2 + H^+ \quad (1)$$

$$[Cu(OH)]^+ + NH_3 \rightarrow Cu^+ - NH_2 + H_2O \quad (2)$$

$$2Cu^+ - NH_2 \rightarrow 2Cu^+ + N_2H_4 \rightarrow 2Cu^+ + N_2 + 2H_2 \quad (3)$$

$$2Cu^+ - NH_2 + 2NH_3 \rightarrow 2Cu^+ + 2N_2 + 5H_2 \quad (4)$$

$$2Cu^{2+} + 4NH_3 \rightarrow 2Cu^+ + 2N_2 + 5H_2 + 2H^+ \quad 2*(1)+(4)=(5)$$

$$2[Cu(OH)]^+ + 4NH_3 \rightarrow 2Cu^+ + 2N_2 + 5H_2 + 2H_2O \quad 2*(2)+(4)=(6)$$

One of the most useful applications for NH_3-TPR is to determine the Cu(II) proportion of total Cu in Cu-SSZ-13 at any given SCR reaction conditions, in a quasi-operando manner. A few in-situ methodologies such as in-situ X-ray absorption near edge structure (XANES)[16], in-situ EPR[14] and in-situ ultraviolet-visible spectrophotometry (UV-vis)[17] have been adopted to quantify Cu species under SCR conditions. However, these techniques are not routinely available in most laboratories. As described earlier, the commonly available H_2-TPR method is not applicable for determining Cu species under conditions relevant to SCR. To demonstrate the applicability of NH_3-TPR in quantifying Cu(II) under such conditions, Cu-SSZ-13 catalyst with 1.34 wt.% Cu(II) content was first exposed to one of three SCR-relevant pretreatment conditions using N_2 as the carrier gas: (1) 500 ppm NH_3 + 5% O_2 + 3% H_2O; (2) 500 ppm NO + 500 ppm NH_3 + 5% O_2 + 3% H_2O; (3) 500 ppm NO + 500 ppm NH_3 + 3% H_2O. Upon arrival of a steady state at 200 °C, the catalyst was rapidly quenched to room temperature (by dousing the sample tube with cold water) with Ar purging to minimize possible reduction of Cu(II) ions by residual NH_3 in the system, followed by an NH_3-TPR test, as illustrated by Fig. 3a. The N_2 release curves with different pretreatments are shown in the inset of Fig. 3a for direct comparison, and deconvoluted curves are shown in Fig. 3b for further analysis. For the sample pretreated with NH_3+O_2+H_2O, two N_2 formation features are distinguished at 205 and 280 °C, similar to those of the O_2-pretreated sample (Fig. 1a) that are readily attributed to $[Cu(OH)]^+$-Z and Cu^{2+}-2Z reduction, respectively. In contrast, new N_2 release peaks at ~250 °C are observed when NO is added into the pretreatment gas flows. These peaks are assigned to the reduction of deposited nitrates (Fig. S8), which act as intermediates or by-products of low-temperature SCR.[18, 19] After subtracting the contribution of nitrates from the total N_2 yields, the relative quantities of $[Cu(OH)]^+$-Z and Cu^{2+}-2Z (in NH_3-solvated forms) with different pretreatments are summarized in Fig. 3c. Setting the Cu(II) content in the oxidized catalyst as 100%, pretreatment in NH_3+O_2+H_2O (followed by quenching) causes ~20% of Cu(II) loss; pretreatment in standard SCR condition causes ~30% Cu(II) loss, and pretreatment in $NO+NH_3+H_2O$ causes ~75% Cu(II) loss. These values show a similar Cu(II) reduction tendency with the report by Paolucci et al.,[16] who determined the Cu(I) proportion in Cu-SSZ-13 under various conditions similar to our pretreatment atmospheres via in-situ XANES and found that $NO+NH_3$ gas mixture effectively reduces Cu(II). To further validate the results shown in Fig. 3c, in-situ EPR was used to quantify Cu(II) during standard SCR reaction followed by O_2 cutoff (Fig. 3d, original spectra shown in Fig. S9). EPR detectable Cu(II) comprises 68% of the total Cu in the catalyst when SCR reaches a steady state at 200 °C, and decreases to 22% after O_2 cutoff. Our NH_3-TPR results are reasonably consistent with the EPR data, suggesting that quenching the catalyst prior to NH_3-TPR largely preserves the various Cu species at steady states. Under low-temperature SCR conditions, the reduction half-cycle of the redox mechanism involves Cu(II) reduction by $NO+NH_3$, as shown by R7 and R8.[3] It is suggested that the reduction of $[Cu(OH)]^+$-Z produces more H_2O (R7), and thus is energetically more favored than the reduction of Cu^{2+}-2Z (R8).[9] We note that in-situ EPR and XANES can hardly distinguish NH_3-solvated $[Cu(OH)]^+$-Z and Cu^{2+}-2Z species in SCR-relevant conditions,[17] while this is readily achievable by NH_3-TPR. Especially, Fig. 3c shows that ~80% initial $[Cu(OH)]^+$-Z is reduced by $NO+NH_3+H_2O$, while the reduction percentage of Cu^{2+}-2Z is only ~65%. These results clearly demonstrate that $[Cu(OH)]^+$-Z is more reducible than Cu^{2+}-2Z in low-temperature SCR.

$$[\mathrm{Cu(OH)}]^+ + \mathrm{NO} + \mathrm{NH_3} \rightarrow \mathrm{Cu}^+ + \mathrm{N_2} + 2\mathrm{H_2O} \quad (7)$$

$$\mathrm{Cu}^{2+} + \mathrm{NO} + \mathrm{NH_3} \rightarrow \mathrm{Cu}^+ + \mathrm{N_2} + \mathrm{H_2O} + \mathrm{H}^+ \quad (8)$$

In summary, NH_3-TPR is established as a quantitative characterization method for Cu(II) ions in Cu-SSZ-13 (likely also in other Cu-zeolites). At low to medium Cu loadings, Cu(II) reduction follows a N_2:Cu stoichiometry of 1:1. Important to SCR studies, the feasibility of NH_3-TPR on determining Cu(II) proportion under quasi-operando conditions is demonstrated, and the different reducibility of two types of Cu(II) ions (*i.e.*, $[Cu(OH)]^+$-Z and Cu^{2+}-2Z) in SCR-relevant conditions is clearly evidenced by NH_3-TPR. This routinely available approach can be readily applied in research on Cu-zeolite SCR catalysts, *e.g.*, in understanding the redox cycling between Cu(II) and Cu(I) in SCR reactions.

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Author contributions

Yue Ma: Conceptualization, Investigation, Writing - original draft. **Xiaodong Wu**: Funding acquisition, Supervision, Writing - review & editing. **Jiancai Ding**: Methodology. **Liping Liu**: Investigation. **Baofang Jin**: Methodology. **Eric D. Walter**: Methodology. **Rui Ran**: Methodology, Supervision. **Zhichun Si**: Methodology. **Feng Gao**: Supervision, Writing - review & editing. **Duan Weng**: Supervision.

Conflicts of interest

There are no conflicts to declare.

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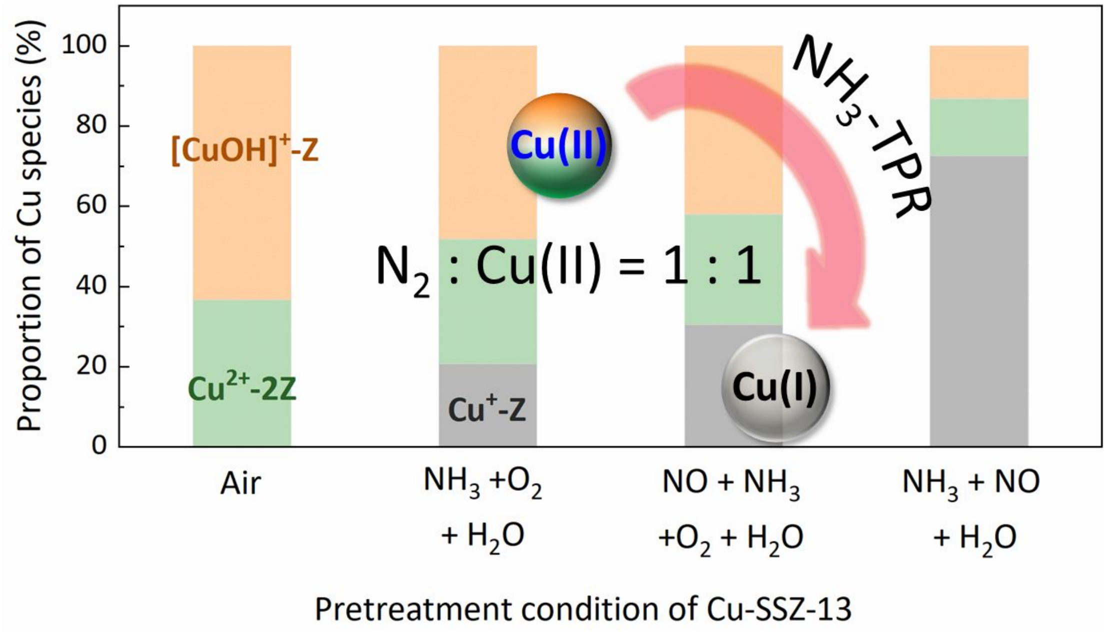

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