Strikingly Distinctive NH_3 -SCR Behavior over Cu-SSZ-13 in the Presence of NO_2

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Article

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Abstract

Commercial Cu-exchanged small-pore SSZ-13 (Cu-SSZ-13) zeolite catalysts are highly active for the selective catalytic reduction (SCR) of NO_x with NH₃, but distinct from other catalyst systems, their activity is unexpectedly inhibited in the presence of NO₂. Here, we combined kinetic experiments, *in-situ/operando* X-ray absorption spectroscopy, and density functional theory (DFT) calculations to obtain direct evidence that under reaction conditions, strong oxidation by NO₂ forces Cu ions to exist mainly as fixed framework Cu²⁺ species (fw-Cu²⁺), which impede the formation of dynamic binuclear Cu⁺ species that serve as the main active sites for the standard SCR (SSCR) reaction. As a result, the SSCR reaction is significantly inhibited by NO₂ in the zeolite system, and the NO₂-involved SCR reaction occurs with an energy barrier higher than that of the SSCR reaction on dynamic binuclear sites. Moreover, the NO₂-involved SCR reaction tends to occur at the Brønsted acid sites (BAS) rather than the fw-Cu²⁺ sites. This work clearly explains the strikingly distinctive selective catalytic behavior in the zeolite system.

Introduction

Increasingly stringent mobile source emission regulations have been pursued around the world to tackle environmental pollution. Nitrogen oxides (NO_x) are inevitable gaseous pollutants emitted from internal combustion engines. Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is the most widely adopted technology to eliminate NO_x.^{1,2} The successful commercialization of Cu-SSZ-13 as an NH₃-SCR catalyst is a significant achievement for diesel engine exhaust post treatment.³ In the past decade, numerous studies have endeavored to uncover the standard SCR (SSCR) reaction mechanism⁴⁻⁷, hydrothermal deactivation mechanism⁸⁻¹¹, and SO₂ poisoning deactivation mechanism¹²⁻¹⁴, and to develop economic and sustainable synthesis methods for Cu-SSZ-13¹⁵⁻¹⁸, bringing about continuous optimization of Cu-SSZ-13 for commercial SCR catalysts.

In actual application, a diesel oxidation catalyst (DOC) is utilized to oxidize carbon monoxide (CO) and hydrocarbons (HCs), accompanied by partial oxidation of NO to NO₂. The formed NO₂ can participate in the NH₃-SCR process through the so-called “fast SCR” reaction (FSCR, reaction 1, consisting of reactions 2 and 3). It is generally believed that the deNO_x efficiency of the FSCR reaction should be higher than that of SSCR (reaction 4) due to bypassing NO oxidation, which is usually the rate-limiting step in the SSCR reaction^{19,20}.

However, there have been few studies reporting that NO_2 measurably promotes the NH_3 -SCR efficiency over Cu-SSZ-13 catalytic systems. On the contrary, inhibition of NO conversion by NO_2 was found over Al-rich Cu-SSZ-13 catalysts due to NH_4NO_3 formation, which is the so-called “abnormal fast NH_3 -SCR reaction”.²¹ In our recent study, we found that the inhibiting effect of NO_2 was closely related to Brønsted acid sites (BASs) and can be alleviated by hydrothermal aging due to the decrease in the number of BASs in Cu-SSZ-13.²² Therefore, we speculated that NO_2 reduction probably occurs at BASs. Also, we previously observed the reaction between NO and NH_4NO_3 occurring at BASs over the H-SSZ-13 catalyst.²³ Furthermore, Kubota et al. found that NO reacts with NH_4NO_3 more rapidly than NH_4NO_3 decomposition over H-AFX and H-CHA zeolites.^{24,25} However, the situation in Cu-containing zeolites is more complicated. More recently, Liu et al. investigated the FSCR mechanism over the Cu-OH site on Cu-CHA zeolite and showed the important role of BASs in the FSCR reaction.²⁶ Currently, little is known about the state and coordination of Cu species under *in-situ/operando* conditions, which is crucial to uncover the SCR reaction mechanism over Cu-based zeolites. Researchers have conducted numerous experimental and theoretical studies to explore the SSCR reaction mechanism in the past decade. Thus, the SSCR mechanism has been relatively clear, in which dynamic binuclear Cu^+ species are the primary active sites.^{4,5,27} However, the influence of NO_2 on the active Cu sites and the mechanism of the NO_2 -involved SCR reaction are barely discussed, and are worth exploring since NO and NO_2 always coexist in actual applications.

In this study, the SCR reaction over the Cu-SSZ-13 catalyst in the presence of both NO and NO_2 was studied by kinetic measurements. *In-situ/operando* X-ray absorption fine structure (XAFS) measurements were applied to reveal the state of copper species under SSCR (only NO as NO_x), FSCR (mixture of equal NO and NO_2 as NO_x) and NO_2 -SCR (only NO_2 as NO_x) reaction conditions. Density functional theory (DFT) calculations were conducted to identify the NO_2 -involved SCR reaction pathways. These results provide new insights into the role of NO_2 in the NH_3 -SCR reaction and shed light on the actual application of Cu-SSZ-13 catalysts in the presence of both NO and NO_2 .

Results And Discussion

Kinetic studies of NO_x conversion under SSCR, FSCR and NO_2 -SCR conditions. We first carried out kinetic studies on the SSCR reaction, with the results shown in Fig. 1. The SSCR rate increases linearly with the square of Cu loading when the Cu loading is below 1.7 wt.% (magnified in Fig. 1b) due to the participation of Cu dimers in O_2 activation, which is consistent with previous studies^{4,5}. The increase trend slows down with further rise in the Cu loading. The turnover frequency (TOF) shows a volcano-type tendency, with a maximum at Cu loading of 1.7 wt.% (Fig. 1c). The increase in TOF at low Cu loading is attributed to the quadratic increase in the SSCR rate. The underutilization of active Cu sites due to mass-transfer limitations results in a decline in TOF at high Cu loading.²⁸ The activation energy (E_a) and pre-exponential factor (A) both increase with the increase in Cu loading, which was also observed by Gao et

al.²⁸ These results can be explained by the transformation of the SSCR from a locally homogeneous reaction to a heterogeneous reaction with increasing Cu loading, in which Cu dimer and Cu monomer species serve as primary active centers, respectively.^{4,28}

Figure S1 shows the NO_x, NO and NO₂ conversion levels over Cu-SSZ-13 with different Cu loadings under steady-state FSCR conditions. We normalized the NO and NO₂ reaction rates by catalyst weight as a function of Cu loading, with the results shown in Fig. 2a and Fig. 2b, respectively. NO reduction was severely suppressed at low temperatures. The extremely low NO conversion at low temperatures was generally thought to be resulted from zeolite pore blocking by the formation of stable NH₄NO₃.^{21,23} Interestingly, the NO₂ reduction markedly decreased with the increase in Cu loading, while it increased as the number of BASs rose at low temperatures (Fig. 2b, 2c and Fig. S2). This demonstrated that the BASs participated in the reduction of NO₂, which was also observed in the NO₂-SCR reaction (Fig. S3). Moreover, the turnover frequency (TOF) of NO₂ on BASs hardly changed as a function of BAS amounts. Fig. S4 presents the NO₂ reaction rate as a function of Cu loading and BASs under NO₂-SCR conditions, which showed the same trend as that with the co-existence of NO and NO₂. The above results indicated that NO₂ primarily reacted at BASs while NO was difficult to be reduced in the presence of NO₂. It is generally known that NO can be effectively reduced at Cu sites. However, the formation of NH₄NO₃ impedes NO access to the active Cu sites. Instead, NO reacts with NH₄NO₃ at BASs to form N₂ through reaction (3). As a result, the NO conversion was relatively low, while NO₂ showed high conversion through reaction with NH₃ to form NH₄NO₃ at low temperatures.

Wavelet transform analysis of in-situ/operando EXAFS measurements. Further, we conducted *in-situ/operando* XAFS experiments on Cu-SSZ-13 samples to uncover the valence state and coordination of copper species under different conditions. Wavelet transform (WT) analysis of extended X-ray absorption fine structure (EXAFS) spectra is a powerful technique to resolve overlapping contributions from different neighbor atoms at close distances around the absorber. As shown in Fig. 3a, the pretreated sample shows a distinct first shell peak at (4.5 Å⁻¹, 1.3 Å), which is associated with contributions from framework oxygen atoms. This result suggested that the copper species mainly exist as fw-Cu²⁺ species, which have high coordination numbers.²⁷ For the second shell sphere (R(Å) > 2 Å), two lobes, at (3.5 Å⁻¹, 2.8 Å) and (6.5 Å⁻¹, 3.3 Å), are well-resolved due to the different backscattering properties of various atoms, which strongly depend on the atomic number. The first lobe is assigned to the second-shell oxygen atom due to the low k value of oxygen atoms. The latter one is attributed to the signals from the Si or Al atoms of the framework. Although some studies attributed the latter lobe to the Cu-Cu contributions in oxygen-bridged Cu dimers,^{29,30} we scarcely observed CuO_x species in X-ray absorption near edge structure (XANES) profiles (Fig. S5a) and did not carry out the procedure of introducing O₂ to NH₃-treated Cu-SSZ-13, to form oxygen-bridged Cu dimers with four NH₃ ligands. Therefore, we deduced that the lobe at 6.5 Å⁻¹ is primarily from the framework Si or Al atoms in the second shell in this work. In fact, the copper species in Cu-SSZ-13 are initially in the solvated state as [Cu(H₂O)_n]²⁺ under ambient conditions, which weakens the

interaction between copper species and the zeolite framework.^{27,31} High-temperature treatment in O₂/N₂ removes the coordinated water molecules and oxidizes copper species to Cu²⁺. As a result, the copper species are in a high valence state and strongly interact with the zeolite framework through electrostatic forces.

After NO adsorption, Cu²⁺ ions are partially reduced, resulting in a slight decrease in the coordination numbers (CNs) of the first shell, denoted by the decrease and weakening of the colored area (Fig. 3b). The lobes resulting from the contributions of the second shell stretched to (3.5 Å⁻¹, 3.1 Å) and (6.5 Å⁻¹, 3.7 Å), respectively. When the pretreated sample was exposed to an NH₃ or NO+NH₃ atmosphere, the signal of the first shell sharply decreased (Fig. 3c and 3d), suggesting that the CNs of the Cu ions significantly declined due to their reduction. Moreover, the two lobes are not well-resolved in the spectra, indicating a decrease in the scattering from the second shell. This is consistent with the formation of dynamic [Cu(NH₃)₂]⁺ species, which is supported by the appearance of feature B in **Fig. S5a** after NH₃ or NO+NH₃ adsorption. After oxidation by O₂ and NO₂, the CNs of the first shell increased to a level similar to that of the pretreated sample, accompanied by the formation of two well-resolved lobes at the second shell (Fig. 3e and 3f). This demonstrated that Cu(NH₃)₂⁺ species are oxidized into Cu²⁺ ions and that the interaction between the Cu²⁺ ions and the zeolite framework is recovered. Compared with oxidation by O₂, oxidation by NO₂ resulted in a higher signal for the lobe at ~6.5 Å⁻¹, indicating that more Cu⁺ species are oxidized into framework-bonded Cu²⁺ ions (fw-Cu²⁺) during the reaction with NO₂.

Figure 4g-4i depicts 2D plots of the WT EXAFS spectra under SSCR, FSCR and NO₂-SCR conditions. Under SSCR conditions, the WT EXAFS spectra resemble the ones in Fig. 3c and 3d. The first shell peak weakened, indicating a decrease in the CNs of Cu species under SSCR conditions. The absence of the lobes at the second shell suggests the easy mobility of the copper complex due to the NH₃ solvation effect. The results proved the existence of large amounts of dynamic Cu(NH₃)₂⁺ species during the SSCR reaction. In the presence of NO₂, however, the CNs of the first shell significantly increased, indicating the oxidation of copper species. Moreover, two well-resolved lobes at the second shell are observed, suggesting that oxidization leads to the copper species becoming closely coordinated with the zeolite framework, which limits their mobility during the SCR reaction. The WT EXAFS spectra are consistent with the Fourier-transformed (FT) EXAFS results (**Fig. S6 and Table S1**), which are discussed in detail in the Supporting Information.

DFT calculation. Next, we used the DFT method to calculate various possible FSCR reaction pathways. There are two possible reaction mechanisms when FSCR occurs at active Cu sites, corresponding to NH₂NO and NH₄NO₃ reaction pathways, respectively. The NH₂NO reaction pathways over isolated [Cu(NH₃)₂]⁺ and dimer Cu ions are shown in **Fig. S7 and S8**, respectively. The reduction process resembles what takes place in the SSCR reaction, in which Cu^{II}OH(NH₃)₂ species are reduced to [Cu(NH₃)₂]⁺ by NH₃ and NO with an energy barrier of 0.32 eV, accompanied by the formation of two H₂O

and one N_2 .^{4,5} By contrast, the reduced $[Cu(NH_3)_2]^+$ species are oxidized by NO_2 rather than O_2 . The rate-determining steps involve the reduction of $Cu^{2+}(NH_3)_2NO_2$, with high energy barriers of 1.65 and 1.58 eV for Cu monomer and dimer, respectively. This result is comparable with the value reported by Janssens et al.³² More details regarding the reaction pathway of intermediate NH_2NO decomposition are shown in **Fig. S9**.

Given the experimental result that NH_4NO_3 forms easily during the FSCR reaction, we next show the results of the NH_4NO_3 reaction pathway on Cu active sites and BASs in Fig. 4 and 5, respectively. The fw- $Cu^{2+}OH$ structure is used as the active site since fw- $Cu^{2+}OH$ dominates during the FSCR and NO_2 -SCR reactions, as indicated by the operando XAFS results (**Fig. S6**). As shown in Fig. 4, fw- $Cu^{2+}OH$ first adsorbs an NH_3 molecule to reach a coordinatively saturated state, which interacts with NO_2 to form an HNO_3 molecule without any energy barrier. The B species is actually considered to be NH_4NO_3 adsorbed on Cu sites. Next, the adsorbed HNO_3 reacts with NO from the gas phase with an energy barrier of 0.87 eV, resulting in the formation of adsorbed HNO_2 and the release of an NO_2 molecule (C→D). Then, the adsorbed HNO_2 reacts with the NH_3 ligand to generate NH_2NO and H_2O . NH_2NO is easily decomposed into N_2 and H_2O through a series of H-migration and isomerization processes (**Fig. S9**).³³ As the desorption of N_2 and H_2O molecules occurs, NH_3 and NO_2 are adsorbed at the Cu site and react to generate NH_2NO and -OH groups. With the decomposition of NH_2NO into N_2 and H_2O , the fw- $Cu^{2+}OH$ site is regenerated. The rate-determining step of the FSCR cycle over the fw- $Cu^{2+}OH$ site corresponds to the reaction of adsorbed HNO_2 with NH_3 ligand to produce NH_2NO and H_2O (E→F), with an energy barrier of 1.58 eV.

The FSCR reaction pathway at BASs is displayed in Fig. 5. NH_3 is adsorbed on the BASs to form NH_4^+ species. Two NO_2 molecules interact with the NH_4^+ species to form NH_4NO_3 species and release an NO molecule without any energy barrier (B→C). The release of NO was also observed in our previous studies during NO_2 adsorption on H-SSZ-13 zeolite.³⁴ Then, NO interacts with an NH_3 from the gas phase to form an $NH_3\cdots NO$ complex, which further reacts with NH_4NO_3 to form NH_4^+ , HNO_3 , and NH_2NO via an H-migration process (C→D). NH_2NO is decomposed into N_2 and H_2O . Subsequently, HNO_3 reacts with NO from the gas phase, resulting in the formation of HNO_2 and the release of an NO_2 molecule (G→H). Reaction between HNO_2 and NH_4^+ species leads to the formation of an $NH_3\cdots NO$ complex and an H_2O molecule. The $NH_3\cdots NO$ complex transfers an H atom to regenerate the BAS and changes into NH_2NO , which then decomposes into N_2 and H_2O . The whole catalytic cycle is completed. The overall energy barrier of the FSCR over the Brønsted acid site is 1.27 eV, which corresponds to the reaction between NH_4NO_3 and the $NH_3\cdots NO$ complex, much lower than that over various Cu sites. The DFT-calculated results indicate that the FSCR process in the SSZ-13 zeolite system tends to occur at BASs.

In summary, we found that NO_2 leads a deep oxidation of copper species as fw- Cu^{2+} , which significantly inhibits the locally homogeneous SSCR over dynamic dimer Cu sites by combining analysis of *in*

situ/operando spectroscopic measurements with DFT calculations demonstrates. As a result, the FSCR reaction occurs primarily at the BASs even though it has a higher energy barrier (1.27 eV) than the locally homogeneous SSCR reaction (about 1.0 eV³²). This work reveals the origin of the abnormal NH₃-SCR behavior over the commercial Cu-SSZ-13 catalyst in the presence of NO₂.

Methods

Sample preparation. The initial Cu-SSZ-13 zeolite was *in-situ* synthesized by a one-pot method.¹⁵ Due to the excess Cu in the initial product, aftertreatments were required to optimize the Cu contents and distribution. In detail, the as-synthesized Cu-SSZ-13 was post-treated with 0.1 mol/L HNO₃ at 80°C for 12 h to remove CuO_x species. After calcination at 600°C, the sample was stirred in NH₄NO₃ solution (0.01 ~ 0.2 mol/L) at 40°C for the second post-treatment process, followed by filtration, washing, drying and calcination at 600°C. The obtained Cu-SSZ-13 catalysts were Al-rich zeolites with Si/Al of ~5 and various Cu loading from 0.4 to 3.8 wt.% (**Table S2**).

Catalyst evaluation. The standard SCR (SSCR), fast SCR (FSCR) and slow SCR (NO₂-SCR) reactions were carried out in a fixed-bed flow reactor system with an online Nicolet Is50 spectrometer, which was used to detect the concentration of reactants and products. The SSCR conditions included 500 ppm NO and 500 ppm NH₃; the FSCR conditions included 250 ppm NO, 250 ppm NO₂ and 500 ppm NH₃; the NO₂-SCR conditions included 300 ppm NO₂ and 500 ppm NH₃. All the conditions included 5% H₂O, 5%O₂ and N₂ balance. The total flow rate was 500 mL/min. The NO_x (NO and NO₂) conversion was calculated at steady state:

$NO_{conversion} = \left(1 - \frac{[NO]_{out}}{[NO]_{in}} \right) \times 100\%$	(1)
$NO_2_{conversion} = \left(1 - \frac{[NO_2]_{out}}{[NO_2]_{in}} \right) \times 100\%$	(2)
$NO_x_{conversion} = \left(1 - \frac{[NO]_{out} + [NO_2]_{out}}{[NO]_{in} + [NO_2]_{in}} \right) \times 100\%$	(3)

To conduct the kinetic studies, the high gas hourly space velocity (GHSV) was controlled by adjusting the catalyst weight. The GHSV of SSCR, FSCR and NO₂-SCR were about ~800,000 h⁻¹, ~1,000,000 h⁻¹ and ~2,000,000 h⁻¹, respectively. The reaction rates (r) in this study are normalized by catalyst weight based on equation (1). The activation energies (E_a) were calculated by the Arrhenius equation (2).

$$r = \frac{F_{NO_x} \cdot X_{NO_x}}{W_{cat}} \quad (1)$$

$$r = [NO_x]_0 A e \left(-\frac{E_a}{RT} \right) \quad (2)$$

where F_{NO_x} represents the NO_x flow rate (mol/s), X_{NO_x} represents the NO_x conversion, W_{cat} is the mass of the catalyst (g), and $[NO_x]_0$ is inlet concentration of NO_x . NO_x represents the NO, NO_2 or both.

Characterizations. The elemental composition of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). N_2 adsorption-desorption analysis of the samples was conducted on a Micromeritics ASAP 2020 instrument. The acid site distribution and contents were measured by NH_3 temperature-programmed desorption (NH_3 -TPD) using the NH_3 -SCR activity measurement instrument. Samples of about 30 mg were used and pretreated in 10% O_2/N_2 at 500 °C for 30 min before cooling down to 120 °C. Then, the gas was changed to 500 ppm NH_3/N_2 for 60 min, followed by N_2 purging for 60min. Finally, the temperature was raised to 700 °C at a rate of 10 °C/min.

The *in situ/operando* X-ray absorption fine structure (*in situ/operando* XAFS) experiments were performed in the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF). The absorption data from -200 eV to 800 eV of the Cu K-edge (8979 eV) were collected. The sample was first pretreated in O_2/He at 500 °C for 30 min before decreasing the temperature to 200 °C, after which the Pre. spectra were collected. Then, the sample was exposed to 500 ppm NH_3/He , 500 NO/He and 500 ppm NH_3/He + 500 ppm NO/He for 60 min, respectively, and spectra were collected. After reduction by $(NO+NH_3)/He$, the sample was exposed to 5% O_2/N_2 and 500 ppm NO_2/N_2 for 60 min, respectively, to obtain the absorption data for the oxidized sample. Moreover, the operando absorption data were collected after the pretreated samples were exposed to SSCR, FSCR and NO_2 -SCR atmospheres for 60 min. The X-ray absorption near-edge structure (XANES) data were background-corrected and normalized using the Athena module implemented in the IFFEFIT software package.³⁵ Extended X-ray absorption fine structure (EXAFS) data were analyzed and fitted using Athena and Artemis ($3.0 < k < 13.0 \text{ \AA}^{-1}$). An amplitude reduction factor (S_0^2) of 0.85 was used for all the fitted data sets. Wavelet transform (WT) analysis of the EXAFS was performed to precisely investigate the local coordination environment of copper species.

Computational details. Spin-polarized periodic DFT calculations were carried out with the Vienna *ab initio* simulation package (VASP 5.4.4)³⁶ The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation was adopted with van der Waals correction proposed by Grimme (i.e., DFT-D3 method)³⁷. The Kohn-Sham orbitals were expanded with a plane-wave basis set with a cutoff energy of 500 eV, and the plane augmented wave (PAW) method was used to describe the interaction between the valence electrons and the cores³⁸. The DFT + U method was applied to Cu 3d states with the values of $U_{eff} = 6.0$ eV to describe the on-site Coulomb interactions^{33,39}. During geometrical optimization, the self-consistent-

field electronic energies were converged to 1×10^{-5} eV and all other atoms were fully relaxed until the maximum force on the atoms was less than 2×10^{-2} eV/Å. The Brillouin zone was sampled with a Monkhorst-Pack k-point grid of $1 \times 2 \times 2$. The Gaussian smearing method was utilized, with a smearing width of 0.2 eV. The transition states of elementary steps were located using the climbing image nudged elastic band (CI-NEB) method with several intermediate images between initial and final states^{40,41}. Thermodynamic data were processed with the VASPKIT code⁴² and the Gibbs free energies are calculated at 200 °C. The SSZ-13 zeolite structure was modelled using two rhombohedral unit cells (24 tetrahedral atoms) with size of 18.84 Å×9.42 Å×9.42 Å (**Figure S10**). One Si atom was replaced by one Al atom in each double 6-membered ring, resulting in a model with Si/Al ratio of 11. One H atom was introduced onto one of the O atoms connected with each Al atom to keep the structure charge-neutral. Based on previous studies^{4,33}, the present computational settings and models were reliable for investigating the NH₃-SCR mechanism over Cu-SSZ-13 zeolites.

Declarations

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References

1. Zhang, R., Liu, N., Lei, Z. & Chen, B. Selective Transformation of Various Nitrogen-Containing Exhaust Gases toward N₂ over Zeolite Catalysts. *Chem. Rev.* **116**, 3658–3721 (2016).
2. Han, L. et al. Selective Catalytic Reduction of NO_x with NH₃ by Using Novel Catalysts: State of the Art and Future Prospects. *Chem. Rev.* **119**, 10916–10976 (2019).
3. Kwak, J. H., Tonkyn, R. G., Kim, D. H., Szanyi, J. & Peden, C. H. F. Excellent activity and selectivity of Cu-SSZ-13 in the selective catalytic reduction of NO_x with NH₃. *J. Catal.* **275**, 187–190 (2010).
4. Gao, F., Mei, D., Wang, Y., Szanyi, J. & Peden, C. H. Selective Catalytic Reduction over Cu/SSZ-13: Linking Homo- and Heterogeneous Catalysis. *J. Am. Chem. Soc.* **139**, 4935–4942 (2017).
5. Paolucci, C. et al. Dynamic multinuclear sites formed by mobilized copper ions in NO_x selective catalytic reduction. *Science* **357**, 898–903 (2017).
6. Hu, W. et al. On the Redox Mechanism of Low-Temperature NH₃-SCR over Cu-CHA: A Combined Experimental and Theoretical Study of the Reduction Half Cycle. *Angew. Chem. Int. Ed.* **60**, 7197–

- 7204 (2021).
7. Paolucci, C. et al. Isolation of the Copper Redox Steps in the Standard Selective Catalytic Reduction on Cu-SSZ-13. *Angew. Chem. Int. Ed.* **126**, 12022–12027 (2014).
 8. Kim, Y. J. et al. Hydrothermal stability of CuSSZ13 for reducing NO_x by NH₃. *J. Catal.* **311**, 447–457 (2014).
 9. Gao, F. & Szanyi, J. On the hydrothermal stability of Cu/SSZ-13 SCR catalysts. *Appl. Catal. A* **560**, 185–194 (2018).
 10. Shan, Y. et al. Precise control of post-treatment significantly increases hydrothermal stability of in-situ synthesized Cu-zeolites for NH₃-SCR reaction. *Appl. Catal. B* **266**, 118655 (2020).
 11. Ye, X. et al. Deactivation of Cu-exchanged Automotive Emissions NH₃-SCR Catalysts Elucidated with Nanoscale Resolution using Scanning Transmission X-ray Microscopy. *Angew. Chem. Int. Ed.* **59**, 15610–15617 (2020).
 12. Hammershøi, P. S., Jangjou, Y., Epling, W. S., Jensen, A. D. & Janssens, T. V. W. Reversible and irreversible deactivation of Cu-CHA NH₃-SCR catalysts by SO₂ and SO₃. *Appl. Catal. B* **226**, 38–45, (2018).
 13. Jangjou, Y. et al. Nature of Cu Active Centers in Cu-SSZ-13 and Their Responses to SO₂ Exposure. *ACS Catal.* **8**, 1325–1337 (2018).
 14. Mesilov, V. V. et al. Differences in oxidation-reduction kinetics and mobility of Cu species in fresh and SO₂-poisoned Cu-SSZ-13 catalysts. *Appl. Catal. B* **284**, 119756 (2021).
 15. Ren, L. et al. Designed copper-amine complex as an efficient template for one-pot synthesis of Cu-SSZ-13 zeolite with excellent activity for selective catalytic reduction of NO_x by NH₃. *Chem. Commun.* **47**, 9789–9791 (2011).
 16. Zhang, L. et al. Recent advances in the preparation of zeolites for the selective catalytic reduction of NO_x in diesel engines. *React. Chem. Eng.* **4**, 975–985 (2019).
 17. Han, J. F. et al. Rapid synthesis and NH₃-SCR activity of SSZ-13 zeolite via coal gangue. *Green Chem.* **22**, 219–229 (2020).
 18. Zhao, Z. et al. Cu-exchanged Al-rich SSZ-13 zeolite from organotemplate-free synthesis as NH₃-SCR catalyst: Effects of Na⁺ ions on the activity and hydrothermal stability. *Appl. Catal. B* **217**, 421–428 (2017).
 19. Iwasaki, M. & Shinjoh, H. A comparative study of “standard”, “fast” and “NO₂” SCR reactions over Fe/zeolite catalyst. *Appl. Catal. A* **390**, 71–77 (2010).
 20. Grossale, A., Nova, I., Tronconi, E., Chatterjee, D. & Weibel, M. NH₃–NO/NO₂ SCR for Diesel Exhausts Aftertreatment: Reactivity, Mechanism and Kinetic Modelling of Commercial Fe- and Cu-Promoted Zeolite Catalysts. *Top. Catal.* **52**, 1837–1841 (2009).
 21. Xie, L., Liu, F., Liu, K., Shi, X. & He, H. Inhibitory effect of NO₂ on the selective catalytic reduction of NO_x with NH₃ over one-pot-synthesized Cu–SSZ-13 catalyst. *Catal. Sci. Technol.* **4**, 1104–1110

- (2014).
22. Shan, Y. et al. Hydrothermal aging alleviates the inhibition effects of NO₂ on Cu-SSZ-13 for NH₃-SCR. *Appl. Catal. B* **275**, 119105 (2020).
 23. Shan, Y. et al. Effects of NO₂ Addition on the NH₃-SCR over Small-Pore Cu-SSZ-13 Zeolites with Varying Cu Loadings. *J. Phys. Chem. C* **122**, 25948–25953 (2018).
 24. Kubota, H. et al. Formation and Reactions of NH₄NO₃ during Transient and Steady-State NH₃-SCR of NO_x over H-AFX Zeolites: Spectroscopic and Theoretical Studies. *ACS Catal.* **10**, 2334–2344 (2020).
 25. Liu, C. et al. In Situ/Operando IR and Theoretical Studies on the Mechanism of NH₃-SCR of NO/NO₂ over H-CHA Zeolites. *J. Phys. Chem. C* **125**, 13889–13899 (2021).
 26. Liu, C. et al. Mechanism of NH₃-Selective Catalytic Reduction (SCR) of NO/NO₂ (Fast SCR) over Cu-CHA Zeolites Studied by In Situ/Operando Infrared Spectroscopy and Density Functional Theory. *J. Phys. Chem. C* **125**, 21975–21987 (2021).
 27. Paolucci, C. et al. Catalysis in a Cage: Condition-Dependent Speciation and Dynamics of Exchanged Cu Cations in SSZ-13 Zeolites. *J. Am. Chem. Soc.* **138**, 6028–6048 (2016).
 28. Gao, F. et al. Understanding ammonia selective catalytic reduction kinetics over Cu/SSZ-13 from motion of the Cu ions. *J. Catal.* **319**, 1–14 (2014).
 29. Negri, C. et al. Structure and Reactivity of Oxygen-Bridged Diamino Dicopper(II) Complexes in Cu-Ion-Exchanged Chabazite Catalyst for NH₃-Mediated Selective Catalytic Reduction. *J. Am. Chem. Soc.* **142**, 15884–15896 (2020).
 30. Sushkevich, V. L., Safonova, O. V., Palagin, D., Newton, M. A. & van Bokhoven, J. A. Structure of copper sites in zeolites examined by Fourier and wavelet transform analysis of EXAFS. *Chem. Sci.* **11**, 5299–5312 (2020).
 31. Song, J. et al. Toward Rational Design of Cu/SSZ-13 Selective Catalytic Reduction Catalysts: Implications from Atomic-Level Understanding of Hydrothermal Stability. *ACS Catal.* **7**, 8214–8227 (2017).
 32. Janssens, T. V. W. et al. A Consistent Reaction Scheme for the Selective Catalytic Reduction of Nitrogen Oxides with Ammonia. *ACS Catal.* **5**, 2832–2845 (2015).
 33. Chen, L. et al. A Complete Multisite Reaction Mechanism for Low-Temperature NH₃-SCR over Cu-CHA. *ACS Catal.* **10**, 5646–5656 (2020).
 34. Liu, K. et al. Quantitative determination of the Cu species, acid sites and NH₃-SCR mechanism on Cu-SSZ-13 and H-SSZ-13 at low temperatures. *Catal. Sci. Technol.* **10**, 1135–1150 (2020).
 35. Newville, M. Interactive XAFS Analysis and FEFF Fitting. *J. Synchrotron Rad.* **8**, 322–324 (2001).
 36. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15–50 (1996).
 37. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **27**, 1787–1799 (2006).

38. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775 (1999).
39. Chen, L., Janssens, T. V. W. & Gronbeck, H. A comparative test of different density functionals for calculations of NH₃-SCR over Cu-Chabazite. *Phys. Chem. Chem. Phys.* **21**, 10923–10930 (2019).
40. Henkelman, G., Uberuaga, B. P. & Jonsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* **113**, 9901–9904 (2000).
41. He, G. et al. Polymeric vanadyl species determine the low-temperature activity of V-based catalysts for the SCR of NO_x with NH₃. *Sci. Adv.* **4**, eaau4637 (2018).
42. Wang, V., Xu, N., Liu, J., Tang, G. & Geng, W. VASPKIT: A Pre- and Post-Processing Program for VASP Code. *arXiv preprint arXiv:1908.08269* (2019).

Figures

Figure 1

SSRC reaction rates as a function of (a) Cu loading and (b) the square of Cu loading. (c) SSRC turnover frequencies (TOF) as a function of Cu loading. (d) Activation energies (E_a) and pre-exponential factors (A) with different Cu loadings.

Figure 2

(a) NO reaction rates as a function of Cu loading over Cu-SSZ-13 catalysts in the NO and NO₂ gas mixtures. (b) NO₂ reaction rates as a function of Cu loading over Cu-SSZ-13 in the NO and NO₂ gas mixtures. (c) NO₂ reaction rates as a function of BASs over Cu-SSZ-13 in the NO and NO₂ gas mixtures. (d) NO₂ turnover frequencies (TOFs) as a function of BASs in the NO and NO₂ gas mixtures.

Figure 3

WT plots for EXAFS spectra of Cu-SSZ-13 treated under different conditions. (a) Cu-SSZ-13 pretreated in O₂/He; (b) NO adsorption; (c) NH₃ adsorption; (d) NO+NH₃ adsorption; (e) NO+NH₃ co-adsorption followed by reaction with O₂; (f) NO+NH₃ co-adsorption followed by reaction with NO₂; (g) SSCR conditions; (h) FSCR conditions; (i) NO₂-SCR conditions.

Figure 4

Gibbs free energy profile of the fast SCR cycle at Cu-OH site as well as optimized geometries of the reactants, transition states (TSS), intermediates, and products for all elementary steps. Except for the two O atoms linked to the Cu-OH group, all other atoms of the zeolite framework are omitted for clarity. Orange, red, blue, and white circles denote Cu, O, N, and H atoms, respectively.

Figure 5

Gibbs free energy profile of the fast SCR cycle at BAS as well as optimized geometries of the reactants, TSs, intermediates, and products for all elementary steps. Except for the Si and Al atoms linked to the OH group, all other atoms of the zeolite framework are omitted for clarity. Yellow and pink circles denote Si and Al atoms, respectively. All other legends are the same as those in Figure 4.

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