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Regulating NO₂ adsorption at ambient temperature by manipulating copper species as binding sites in copper-modified SSZ-13 zeolites

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ABSTRACT: Atmospheric NO₂ pollution poses significant risks to human health and the environment even at low concentrations, necessitating the development of efficient technologies for its removal under ambient conditions. This study developed copper (Cu)-modified SSZ-13 zeolites (referred to as CuⁿSSZ-13 where n represents the valence state of Cu) for NO₂ removal by adsorption. CuⁿSSZ-13 zeolites containing Cu species with different valence states and proportions were prepared by reducing Cu²⁺-exchanged SSZ-13 zeolite (Cu²⁺SSZ-13) using H₂ at different temperatures. The CuⁿSSZ-13 reduced at 190 °C showed the highest NO₂ removal capacity (1.79 mmol/g), outperforming pristine SSZ-13 and Cu²⁺SSZ-13 by 52.3% and 19.4%, respectively. The improvement was due to the increased amount of adsorption sites (Cu⁺ and H⁺) and the stronger affinity of Cu⁺ than Cu²⁺ towards NO₂, as confirmed by density functional theory (DFT) calculations. The generation of Cu⁰ nanoparticles and moisture in zeolites during reduction were undesirable for NO₂ adsorption. However, this could be eliminated by lowering the reduction temperature and applying a thermal activation, respectively. This work provides systematical methods for designing zeolite adsorbents for ambient NO₂ removal and offers insights into the burgeoning field of air pollution control.

1. Introduction

Nitrogen oxides (NO_x), including NO and NO₂, are intensively exhausted from mobile and stationary sources such as vehicles and industries. NO_x have raised public concerns due to their detrimental effects on both human health and eco-systems.¹⁻³ For example, NO_x can interact with other air pollutants such as volatile organic compounds (VOCs) under sunlight, leading to the formation of secondary pollutants such as smog and highly irritating gas.⁴⁻⁶ Meanwhile, NO_x themselves, as toxic components, can directly affect human health by decreasing lung function and causing respiratory symptoms, even at low concentrations.⁷ As NO₂ is more active and around 30 times more toxic than NO,⁸ NO₂ is categorized as a criteria pollutant representing NO_x. Thus, the atmospheric NO₂ pollution and its control have attracted increased attention in recent decades, particularly in densely populated urban areas. For example, the concentration of roadside NO₂ in Hong Kong remains at a harmful level (80 ug/m³),⁹ which is twice the World Health Organization (WHO) standard (40 ug/m³).¹⁰ The complex

and congested nature of Hong Kong makes it challenging to dilute the roadside NO₂. Therefore, efforts to abate atmospheric NO₂ should focus on both reducing NO₂ emissions in exhaust gases and removing NO₂ from the ambient air.

De-NO_x technologies, such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR), have been extensively developed and implemented, delivering high efficiency in NO_x removal (99 %).¹¹⁻¹³ However, the operating temperature window (300–1100 °C) of these technologies makes their application prohibitive in low-temperature NO_x (e.g., atmospheric NO_x) abatement. Moreover, the generation of NH₃ (as reductant) by decomposing urea solution at low temperatures (<180 °C) poses a significant challenge for the SCR process.¹⁴ In addition, stricter regulations have increased the urgency for low-temperature NO_x emission control. Adsorption is considered an alternative approach for NO_x removal at low temperature. However, most adsorbents have only been evaluated for NO_x adsorption at temperatures above 80 °C,¹⁵⁻¹⁷ omitting NO₂ adsorption under ambient conditions. Thus, this study aims to develop effective NO₂ adsorbents, with high NO₂ adsorption capacity and selectivity, for atmospheric NO₂ abatement at ambient temperature.

Adsorbents that exhibit a specific affinity towards NO₂ with moderate strength can afford high NO₂ selectivity and capacity, making them desirable for NO₂ adsorption. Given the presence of π bonds in the NO₂ molecule, materials containing transition metal species are promising candidates for NO₂ adsorption due to their unique interaction (π-complexation) with NO₂, which forms π-backdonation from *d* orbital metal center to the π* orbitals of the π-structured molecules.¹⁸ This interaction, with moderate strength, bridges the gap between physisorption and chemisorption, enabling the π-complexation adsorbents to exhibit both high selectivity and good reversibility.¹⁹ Copper (Cu), an affordable and abundant transition metal that has been extensively studied and used in high-temperature NO_x SCR,

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emerges as a promising candidate for NO₂ adsorption.²⁰⁻²⁴ For instance, Cu-contained carbon showed a high NO₂ removal capacity at room temperature, while the low thermal stability of carbon materials causes them to burn readily during regeneration at high temperatures.²⁰ Cu nanoparticles (NPs) loaded silica (KCC-1) has been reported as an effective NO₂ adsorbent, with the highly dispersed Cu NPs serving as effective adsorption sites for NO₂.²⁵ However, the NO₂ adsorption and dissociation on Cu²⁺ and Cu⁺ have not been studied. The Cu-based metal-organic framework (MOFs) showed enhanced NO₂ adsorption due to increased porosity and the reactive adsorption of NO₂ on Cu.²⁴ However, the high cost and low thermal/hydrothermal stability of MOFs limit their applications in real-world gas adsorption processes.

Small-pore zeolites, characterized by their three-dimensional porous structures, high thermal stability, and large surface areas, have extensive applications in gas adsorption and separation.²⁶ Zeolites can also serve as unique ligands that tune the π -complexation between NO₂ and Cu.²⁷ Sierraalta *et al.* have demonstrated that Cu species-contained zeolites showed a stronger affinity towards NO₂ molecules than those containing other transition metals (Ag and Au).²⁸ Onitsuka *et al.* reported that zeolites infused with Cu salts showed enhanced performance in adsorbing NO_x at a low concentration of about 5 ppm.²⁹ Note that extra-framework cations in zeolites are the dominant adsorption sites, whose properties dictate gas adsorption performance.³⁰ For instance, the valence state of these cations can affect NO₂ adsorption performance, particularly the affinity of the adsorbent for NO₂. For specific types of cations, such as Cu, its valence state is directly related to the radius and the occupancy of the valence shell. Compared with Cu²⁺, Cu⁺ and Cu⁰ possess higher valence shell occupancies and fewer constraints (due to the larger radius) on the valence shell electrons, allowing more *d*-orbital electrons to be back donated to the π^* orbital of NO₂. Consequently, the π -complexation formed between NO₂ and Cu ions at lower states (Cu⁺ and Cu⁰) is anticipated to improve gas-host interaction, leading to a higher affinity to NO₂.

Herein, we prepared Cuⁿ⁺SSZ-13 zeolites (n=0, 1, and 2) by reducing the Cu²⁺-exchanged SSZ-13 zeolite under H₂ atmosphere and systematically studied their NO₂ removal performance and mechanisms. Thanks to the formation of Cu⁺ ions and the increased number of adsorption sites, Cuⁿ⁺SSZ-13 zeolites showed enhanced NO₂ uptake and insignificant NO release. This work suggests that the tuning of Cu species as specific binding sites in zeolite could be an effective approach for regulating the affinity of zeolites for NO₂ adsorption.

2. Experimental

2.1 Synthesis

Synthesis of H⁺SSZ-13 (Si/Al=12). The synthesis of H⁺SSZ-13 (Si/Al=12) was conducted following a previously reported method.³¹ Specifically, 39.6 g of N, N, N-trimethyl-1-adamantanamine hydroxide (TMAdaOH, 25 wt%, Sachem Inc.) and 19.5 g of tetraethyl orthosilicate (TEOS, sigma 98%) were mixed with 4.05 g of deionized (DI) water. This mixture was

stirred for 2 h at room temperature in a sealed polypropylene bottle. Afterwards, 1.05 g of aluminum ethoxide (Strem Chemical, 99%) was added to the mixture and stirred for another 1 h. The gel was then transferred into a 100-mL Teflon-lined autoclave and heated at 140 °C under static conditions for 6 days. After the crystallization, the product was filtered, thoroughly washed with DI water, and then dried at 80 °C overnight. Finally, the product was calcined in an air atmosphere at 550 °C for 8 h with a ramping rate of 2 °C/min.

Synthesis of Cu²⁺SSZ-13. The synthesis of Cu²⁺SSZ-13 involved a liquid-phase ionic exchange process, a common approach for incorporating extra-framework cations into zeolites. Typically, 0.5 g of the as-synthesized H⁺SSZ-13 was dispersed in 50 mL of 0.5 M NH₄NO₃ and stirred for 12 h at 80 °C, with the process being repeated four times to ensure thorough ion exchange. The resulting NH₄⁺SSZ-13 product was filtered, thoroughly washed with DI water, and dried at 80 °C overnight. Then, 0.5 g of the as-synthesized NH₄⁺SSZ-13 was dispersed in 50 mL of 0.5 M Cu(NO₃)₂ solution and stirred for 12 h at 80 °C, again being repeated four times. The resulting Cu²⁺SSZ-13 was collected by filtration, washed with extensive DI water, and dried at 353 K overnight.

Synthesis of H₂-reduced Cuⁿ⁺SSZ-13 samples. A series of Cuⁿ⁺SSZ-13 samples were prepared by reducing Cu²⁺SSZ-13 under H₂ atmosphere at various temperatures. H₂-temperature programmed reduction (TPR) was conducted on a Micromeritics ASAP 2950 instrument to identify optimal reduction conditions for the preparation of Cuⁿ⁺SSZ-13. The signal of H₂ during the reduction process was detected by a thermal conductivity detector (TCD). Then, 0.1 g of Cu²⁺SSZ-13 was placed in a tube furnace and thermally treated under Argon at 350 °C (ramping rate = 2 °C/min) for 4 h to remove the pre-adsorbed impurities. After cooling to room temperature, 5 % H₂ (balanced with Ar, 20 cc/min) was continuously purged and Cu²⁺SSZ-13 was heated at 100 °C to 700 °C for 3 h (ramping rate = 2 °C/min). The resulting products are named Cuⁿ⁺SSZ-13-reducing temperature-R (e.g., Cuⁿ⁺SSZ-13-100-R).

2.2 Characterizations

Synchrotron powder X-ray diffraction (PXRD) was measured by a Mythen-II detector at the PD beamline, Australian Synchrotron, ANSTO. To understand the valence state and the coordination environment of the Cu ions in Cuⁿ⁺SSZ-13 samples, Cu K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were collected at the XAS beamline, Australian Synchrotron, ANSTO. The morphologies of the samples were investigated by a scanning electron microscope (SEM) (EVO MA10, ZEISS, Germany). The specific surface area and pore volume of Cuⁿ⁺SSZ-13-190-R before and after NO₂ dynamic column adsorption, as well as fresh H⁺SSZ-13, were determined by a 3Flex Surface Characterization Analyzer (Micromeritics Instrument Corp., U.S.A.) using N₂ at -196 °C. Prior to measurement, the samples were degassed on the 3Flex Surface Characterization Analyzer at 300 °C for 3 h. The chemical composition (e.g., Si/Al and metal/Al ratios) of the samples was determined by Energy dispersive spectroscopy (EDX) using an EDX detector (Oxford Aztec Energy X-MAX 50) equipped in SEM



(FEI Quanta 450 FEG). The in-situ Fourier Transform Infrared (FTIR) spectra of Cuⁿ⁺SSZ-13-190-R were recorded on an IRAffinity-1 FTIR spectrophotometer (Shimadzu, Japan) at 25 °C, with a NO₂ concentration of 1000 ppm and a flow rate of 60 mL/min. Before the measurement, Cuⁿ⁺SSZ-13-190-R was thermally treated in the FTIR cell under a N₂ atmosphere at 200 °C for 8 h to remove the pre-adsorbed gases and moisture.

2.3 Fixed-bed NO₂/NO dynamic column adsorption at room temperature.

The dynamic column breakthrough (DCB) of NO_x was measured using a fixed-bed system (Fig. S1) under ambient conditions (25 °C, 1 bar). The adsorbent (0.1 g) was well mixed with non-reactive glass beads (3 mm in diameter) to generate a homogeneous bed, and then packed into a stainless-steel tube. Unless otherwise specified, the samples were degassed at 300 °C under Argon before NO_x adsorption until the pre-adsorbed moisture was completely removed, as monitored by a Mass Spectrometer (Stanford Research Systems UGA300). Subsequently, NO₂ or NO (both 1000 ppm) in helium was purged through the column at a total inlet flow rate of 60 mL/min at 25 °C. The concentrations of NO₂ and NO in the outlet gas were measured using an electrochemical sensor (RAE Systems, MultiRAE Plus PGM-50/5P).

2.4 Density functional theory (DFT) calculation

DFT calculations were performed using the QUANTUM ESPRESSO package.³²⁻³⁵ Ultrasoft pseudopotentials with the Perdew-Burke-Ernzerhof exchange-correlation functional were employed.³⁶ The planewave cutoffs were 30 Ry and 240 Ry for wavefunctions and the augmented charge density, respectively. The semiempirical Grimme's DFT-D3 scheme was used for Van der Waals interaction correction.³⁷ The SSZ-13 zeolite has a 1×1×1 supercell with a total trigonal P supercell size of 13.675 Å × 13.675 Å × 14.767 Å. Three Si atoms were replaced with Al atoms. To maintain the charge balance, hydrogen atoms were added near the Al atoms according to the charge of the inserted transition metal ions. The 6-membered ring (6MR) has been identified as the most favorable location for the extra-framework cations.³⁸ Thus, we examined the local structures of the Cu ions in the 6MR, with 2 Si atoms being replaced by 2 Al atoms.

3. Results and discussion

3.1 Characterizations of adsorbents

Cu²⁺SSZ-13 was prepared from H⁺SSZ-13 by an ion-exchange method, where Cu²⁺ substituted the extra-framework H⁺ cations (Fig. 1a). The synchrotron PXRD patterns of Cu²⁺SSZ-13 indicated the high purity and crystallinity characteristic of chabazite (CHA)-type SSZ-13 zeolite (Fig. 1b). As displayed in the SEM image (Fig. 1c), Cu²⁺SSZ-13 particles possess an elliptical shape and smooth exterior surfaces. Cuⁿ⁺SSZ-13 zeolites were then prepared by reducing Cu²⁺SSZ-13 under H₂. Prior to the reduction, H₂-TPR was conducted to determine the optimal reduction temperature (Fig. 1d). With the temperature increasing, two H₂ consumption peaks appeared at around 200 and 400 °C, which were attributed to the reduction of Cu²⁺ at various locations within the zeolite.³⁹ It is noteworthy that Cu²⁺

ions at different locations within the zeolite requires different energy levels to be reduced. For example, the six-membered ring (6MR) in CHA is the most stable site for Cu²⁺, demanding more energy for reduction than those situated at an eight-membered ring (8MR).^{40, 41} To achieve varying levels of Cu²⁺ reduction in SSZ-13 zeolite, both low (≤250 °C) and high temperature (≥390 °C) ranges were adopted.

Upon high-temperature reduction (390, 490, and 750 °C), the structure of Cuⁿ⁺SSZ-13 samples remained intact, as evidenced by the unchanged PXRD peak locations of Cuⁿ⁺SSZ-13 and Cu²⁺SSZ-13 (Fig. 2a). However, the undesirable formation of Cu⁰ occurred on the external surface of the zeolite (Fig. 2c). Rietveld refinement of PXRD indicated that the crystallite size of these Cu⁰ particles (17, 23, and 25 nm at 390, 490, and 750 °C, respectively) increased with the elevated reduction temperature (Fig. S2). The X-ray absorption spectroscopy (XAS) results showed that higher reduction temperatures resulted in a shift towards lower energy and a reduction in intensity of the white line peak (Fig. 2b), corresponding to decreases in the valence state and the occupancy of *d* orbitals of Cu ions.⁴² These observations suggest that during the reduction, Cu²⁺ migrated from the supercage to the external surface of zeolites and aggregated to form metallic Cu particles (Fig. 2c). This mitigation process can be explained by the R-plot EXAFS spectra (Fig. 2b, inset). Two peaks appearing at 1.7 Å and 2.2 Å were ascribed to the Cu-O and Cu-Cu bonds, respectively, arising from the coordination of Cu ions with lattice oxygen atoms in zeolite (Cu-O) and Cu-Cu bonds in elementary Cu.⁴³ The intensity of Cu-O peak decreased while the Cu-Cu peak increased upon reduction at higher temperatures, indicating that more Cu²⁺ migrated from the cage to the external surface of zeolite to form elementary Cu. This result is consistent with the reduced lattice parameters of Cuⁿ⁺SSZ-13 at high reduction temperatures (Fig. 2d), which was attributed to the contraction of the zeolite lattice due to negative thermal expansion.⁴⁴

It is acknowledged that the well dispersed extra-framework cations in zeolites serve as the dominant active adsorption sites for gas molecules.^{27, 45, 46} Therefore, the presence of bulk Cu⁰ NPs on the external surface of zeolites should be minimized. Consequently, a further decrease in the reduction temperature was implemented. No characteristic peaks of elementary Cu were observed in the PXRD patterns of Cuⁿ⁺SSZ-13 samples reduced at 100, 150, 170 and 190 °C (Fig. 3a), indicating the absence of Cu⁰. The XAS results showed the changes in Cu²⁺/Cu⁺ levels within zeolites (Fig. 3b). The weak absorption peak ranging between 8975 and 8980 eV is the fingerprint of Cu²⁺, which is assigned to a dipole-forbidden 1s→3d transition.⁴⁷ The characteristic peak of Cu⁺ was observed at 8980–8985 eV, corresponding to the 1s→4p transition.⁴⁸ As the reduction temperature increased, the Cu²⁺ peak at 8978 eV diminished, while the Cu⁺ peak at 8984 eV gradually increased, suggesting that a higher reduction temperature facilitated the conversion of Cu²⁺ to Cu⁺. The edge peak at 8993–8997 eV, known as the 'white line' of Cu²⁺, indicates a higher oxidation state when the peak intensity is greater.⁴⁸ As the reduction temperature increased, the intensity of the white line decreased, further suggesting a transformation of Cu²⁺ to Cu⁺.

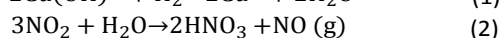
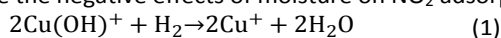


3.2 NO₂ adsorption

The NO₂ adsorption performance of Cuⁿ⁺SSZ-13 reduced at different temperatures (i.e., 100, 150, 170, and 190 °C) was validated by NO₂ dynamic adsorption at room temperature (Fig. 4a). Prior to NO₂ adsorption, the adsorbents were activated at 300 °C under Ar to remove the pre-adsorbed impurities. The NO₂ adsorption capacity of the Cuⁿ⁺SSZ-13 samples increase with the elevated reduction temperature (Fig. 4b), attributed to a higher proportion of Cu⁺ present at a higher reduction temperature. The linear correlation between the NO₂ capacity and the reduction temperature encouraged us to tentatively elevate the reduction temperature to 250 °C, intending to further improve the NO₂ adsorption capacity. However, the NO₂ adsorption over Cuⁿ⁺SSZ-13-250-R was found to be even lower than that of the unreduced sample (Cu²⁺SSZ-13). This result was caused by the formation of Cu⁰ particles on the external surface of zeolite (see SEM image, Fig. S3), which reduced the number of accessible active adsorption sites for NO₂ molecules. The highest NO₂ adsorption capacity, achieved by Cuⁿ⁺SSZ-13-190-R, was 1.79 mmol/g (Fig. 4b). This capacity demonstrated a significant increase of 19.4% and 52.3% with respect to that of Cu²⁺SSZ-13 and pristine H⁺SSZ-13, respectively, substantially surpassing the performance of the reported metal-modified zeolites (Table S1). The above results clearly show that the H₂ reduction of Cu²⁺SSZ-13 effectively improves the NO₂ adsorption capacity, attributed to the increased affinity of binding sites towards NO₂.

To assess the impact of NO₂ adsorption on the specific surface area and pore volume of the Cu-modified zeolite, N₂ adsorption-desorption isotherms were recorded for Cuⁿ⁺SSZ-13-190-R before and after NO₂ dynamic adsorption (Fig. 4c and 4d, Table S2). Post-adsorption, the BET surface area of Cuⁿ⁺SSZ-13-190-R remained largely unchanged, while the pore volume slightly increased from 0.34 to 0.40 cm³/g which was probably due to the formation of additional interparticle stacking pores. Therefore, the porous structures of Cuⁿ⁺SSZ-13-190-R remained largely unaffected after a cycle of NO₂ dynamic adsorption. It is anticipated that the lifespan and adsorption capacity of Cuⁿ⁺SSZ-13-190-R can be substantially preserved by regenerating it through a gentle heating process to drive off adsorbed water and NO₂. Furthermore, in comparison with H⁺SSZ-13 without Cu modification, which featured micropores with a Brunauer–Emmett–Teller (BET) surface area of 771.69 m²/g and a pore volume of 0.38 cm³/g (Fig. S4), Cuⁿ⁺SSZ-13-190-R exhibited a micro-mesoporous structure with a reduced surface area (557.97 m²/g) and pore volume (0.34 cm³/g). Despite the larger surface area and pore volume of the unmodified H⁺SSZ-13, the Cu-modified Cuⁿ⁺SSZ-13-190-R demonstrated a higher NO₂ adsorption capacity. This finding suggests that the incorporation of Cu into the SSZ-13 zeolite significantly enhances the NO₂ adsorption process, playing a more important role than the surface area and pore volume. Therefore, while surface area and pore volume are important factors in adsorption processes, the unique role of Cu within the SSZ-13 zeolite is the key determinant for the improved NO₂ removal performance.

To evaluate the effect of moisture on NO₂ adsorption, experiments were conducted on non-activated Cuⁿ⁺SSZ-13 samples (i.e., without thermal treatment prior to NO₂ adsorption). Compared with Cu²⁺SSZ-13, the non-activated Cuⁿ⁺SSZ-13 samples showed a decreased NO₂ capacity and an increased release of NO (Fig. S5). The decline in capacity was due to the presence of moisture within zeolites generated during the H₂ reduction process (Eqn. 1). Such moisture would poison the active adsorption sites (Cu ions) by forming Cu hydrates and blocking sites intended for NO₂ adsorption, thereby reducing the NO₂ capacity. FTIR analysis (Fig. S6) suggested that the moisture could facilitate NO₂ transformation into NO₃⁻ and gaseous NO (Eqn.2).⁴⁹ After a certain time, the amount of released NO decreased, and the NO release curves stabilized, suggesting the moisture was gradually consumed by NO₂. Therefore, the thermal activation process is essential to mitigate the negative effects of moisture on NO₂ adsorption.



In addition to improving NO₂ capacity, moisture removal also contributed to the decrease of NO release, which was evident from the longer NO retention time and the more gradual slopes of NO release curves (Fig. 4a). However, the correlation between the amount of NO released and the reduction temperature was inconsistent, which resulted from the different NO retention abilities of the samples. For example, Cuⁿ⁺SSZ-13-100-R showed the highest NO adsorption capacity (Fig. 5), aligning with the lowest amount of NO released (Fig. 4b). The NO adsorption capacity decreased with the increasing reduction temperature from 100 to 190 °C, while increased when the reduction temperature was further elevated to 250 °C.

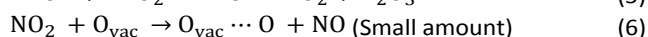
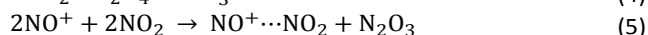
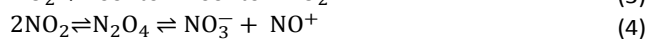
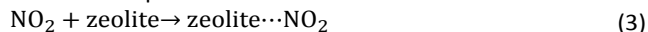
Our Cuⁿ⁺SSZ-13 adsorbent, which exhibits an enhanced capacity for ambient NO₂ abatement yet sensitivity to moisture, can be effectively used for the reduction of NO₂ emission from the engine pipeline when combined with desiccant materials or condensation systems that remove moisture from the exhaust gas. Additionally, our zeolite can be used in air purifiers or industrial settings to remove NO₂, incorporating moisture control mechanisms such as heating elements or moisture-absorbing materials. Given the well-preserved specific surface area and pore volume after NO₂ adsorption, as evidenced by porous property analysis, the Cuⁿ⁺SSZ-13-190-R adsorbent is expected to maintain its performance over multiple cycles of adsorption and thermal regeneration, thereby ensuring a long lifespan in the aforementioned practical applications.

3.3 Discussion of mechanism

To elucidate the mechanism of NO₂ adsorption on our Cu-modified zeolite, in-situ FTIR analysis of the Cuⁿ⁺SSZ-13-190-R zeolite during the NO₂ adsorption process was carried out (Fig. 6). The FTIR spectra revealed the presence of adsorbed NO₂ at 1690 cm⁻¹,⁵⁰ which tended to form N₂O₄ dimer (1261 cm⁻¹)⁵¹ in small-pore zeolites due to the confinement effect.⁴⁵ The adsorbed N₂O₄ can undergo ionization in zeolite to form NO₃⁻ and NO⁺.^{52, 53} As anticipated, the formation of nitrites was observed, including bridging NO₃⁻ (1630 cm⁻¹) and monodentate NO₃⁻ (1534 cm⁻¹).^{54, 55} Meanwhile, an asymmetric band at



around 2178 cm⁻¹, corresponding to two NO⁺ stretches at 2214 and 2178 cm⁻¹, indicative of the generation of NO⁺ intermediates⁵⁶, which can serve as adsorption site for NO₂.⁴⁵ The formation of NO⁺-NO₂ complexes was confirmed by the presence of an N-O stretch at 1741 cm⁻¹ accompanied by another NO stretch at 2109 cm⁻¹,⁵⁶ as well as a weak band at 1925 cm⁻¹ assigned to N₂O₃,⁵⁴ a product of NO₂ adsorption on NO⁺.⁵⁷ Although a small amount of NO was released during NO₂ adsorption due to NO₂ dissociation caused by oxygen vacancies, no distinct FTIR peaks indicative of adsorbed NO were observed. Based on these findings, the mechanism for NO₂ adsorption on the Cuⁿ⁺SSZ-13-190-R zeolite during adsorption was proposed, as shown in Eqn. 3-6.



To understand the effects of copper valence states on NO₂ adsorption in zeolites, DFT calculations were conducted to study the electronic and structural changes associated with Cu⁺ and Cu²⁺ ions upon NO₂ adsorption. As shown in Fig. S7, the number of cations (Cu⁺ and H⁺) in zeolite after H₂ reduction is increased. As the cations would serve as major adsorption sites, the increase in cation density would afford more binding sites for NO₂ adsorption. Moreover, as shown in Table 1, the formation of Cu⁺ (binding energy of 20.06 kcal/mol), which has a higher affinity towards NO₂ than Cu²⁺ (binding energy of 14.36 kcal/mol), strengthens the interaction with NO₂ through π -complexation. Thus, the increase in the density of adsorption sites with elevated binding strength enables elevated NO₂ uptake.

The optimized local structures of NO₂/NO adsorbed on Cu⁺ and Cu²⁺ in SSZ-13 zeolites were analyzed (Fig. 7). When NO₂ or NO is adsorbed, Cu-O bonds are partially disrupted, and the position of Cu ions shifts from a planar arrangement to a non-planar one. These changes in Cu-O coordination numbers and the displacement of Cu ion positions can indicate the intensity of interaction with NO_x. Calculations showed that the reduced electron occupancies (ΔOc) in the 3d orbitals and the increased ΔOc in the 4s and 4p orbitals (Table 2), suggesting the σ -donation from NO₂ and the π -backdonation from Cu ions, respectively. In addition, Cu²⁺ (0.72 Å) has a smaller radius than Cu⁺ (0.96 Å) and attracts the electrons more tightly.²⁶ This constraint resulted in more stable electrons in the d orbitals of Cu²⁺, making it more difficult to form backdonation to the π^* orbital of NO₂ and thus weakening the interaction with NO₂. Thus, the higher affinity of Cu⁺ for NO₂ than Cu²⁺, which is attributed to the more efficient π -complexation, facilitates NO₂ adsorption by Cuⁿ⁺SSZ-13.

Conclusions

In this work, in-depth analysis of NO₂ adsorption on Cuⁿ⁺SSZ-13 zeolites at ambient conditions were conducted, including evaluations of NO₂ uptake, NO release, the affinity of adsorption sites towards NO₂, and the underlying adsorption mechanisms. Among the Cu-modified zeolites investigated,

Cuⁿ⁺SSZ-13-190-R exhibited the highest NO₂ adsorption capacity, outperforming both H⁺SSZ-13 and Cu²⁺SSZ-13. Our experimental and DFT studies demonstrated that the enhanced NO₂ adsorption was attributed to the formation of abundant Cu⁺ ions within the zeolite, which have a higher affinity to NO₂ than Cu²⁺, as well as the increased amount of adsorption sites. The elimination of moisture and Cu⁰ formed upon Cu²⁺SSZ-13 reduction was favorable for NO₂ adsorption. The findings of this research could provide valuable insights for the development of adsorbents for NO₂ removal at ambient temperature.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Figures and tables:

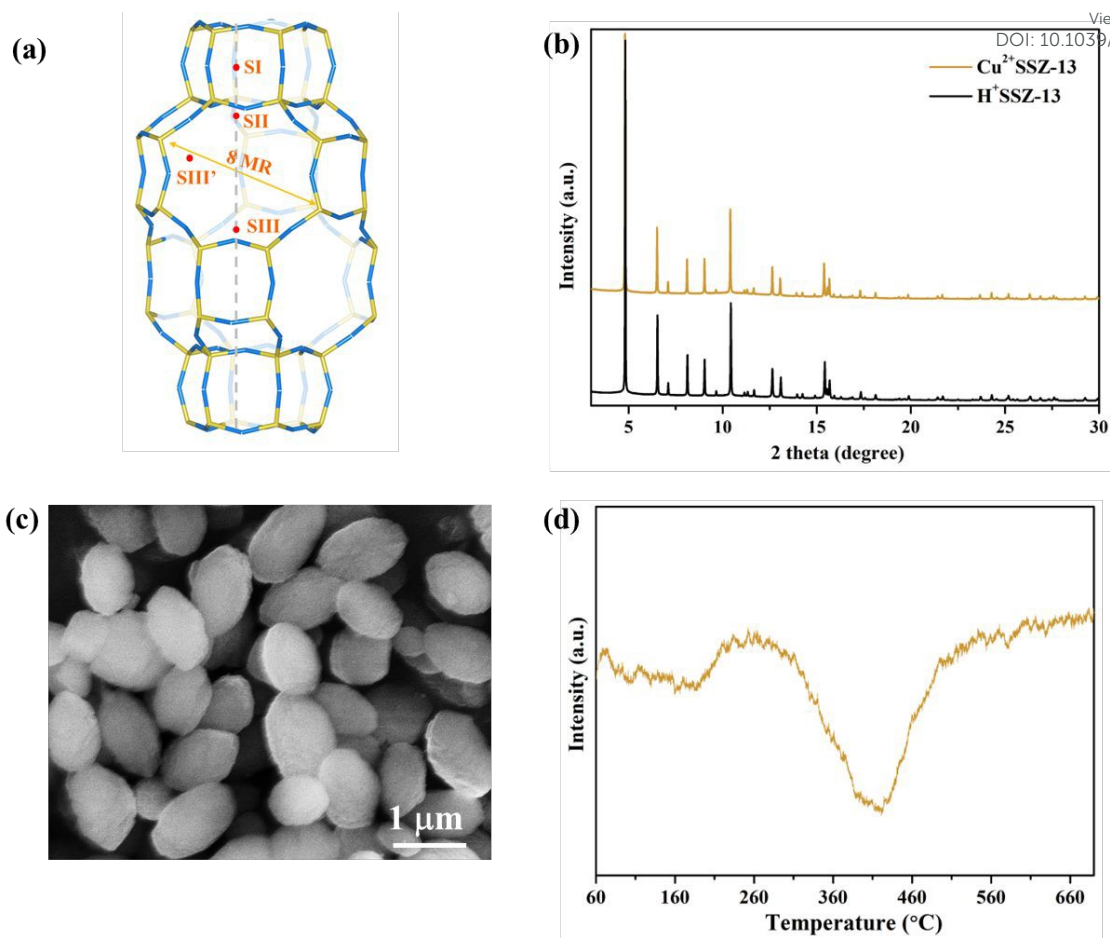


Figure 1. (a) Illustration of the local crystal structure of chabazite (CHA) zeolites. SI–SIII' are the possible positions of extra-framework cations; (b) Synchrotron powder X-ray diffraction patterns of Cu²⁺SSZ-13 and pristine H⁺SSZ-13 (wavelength=0.7735 Å); (c) SEM image of Cu²⁺SSZ-13; and (d) H₂-TPR profile of Cu²⁺SSZ-13.



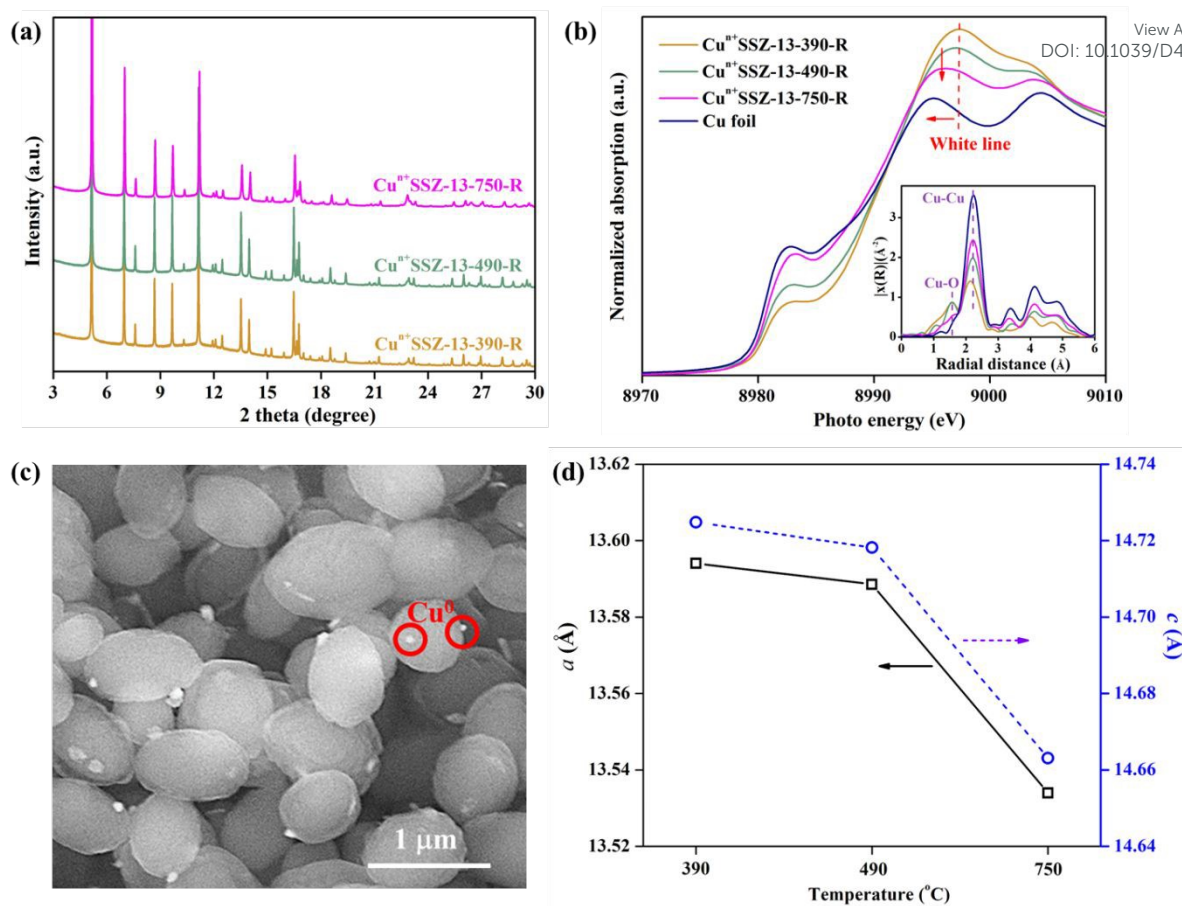


Figure 2. (a) PXRD patterns (wavelength: 0.8275 Å) and (b) Cu K-edge XAS spectra of Cuⁿ⁺SSZ-13 reduced by H₂ at 390, 490, and 750 °C (Inset: Fourier transformed EXAFS modulation with phase correction in the k-range of 3.0–12.5 Å⁻¹, k²-weighted); (c) SEM image of Cuⁿ⁺SSZ-13-390-R; and (d) Variation of unit cell parameters (*a* and *c*) of Cuⁿ⁺SSZ-13 in relation to the H₂-reduction temperature.



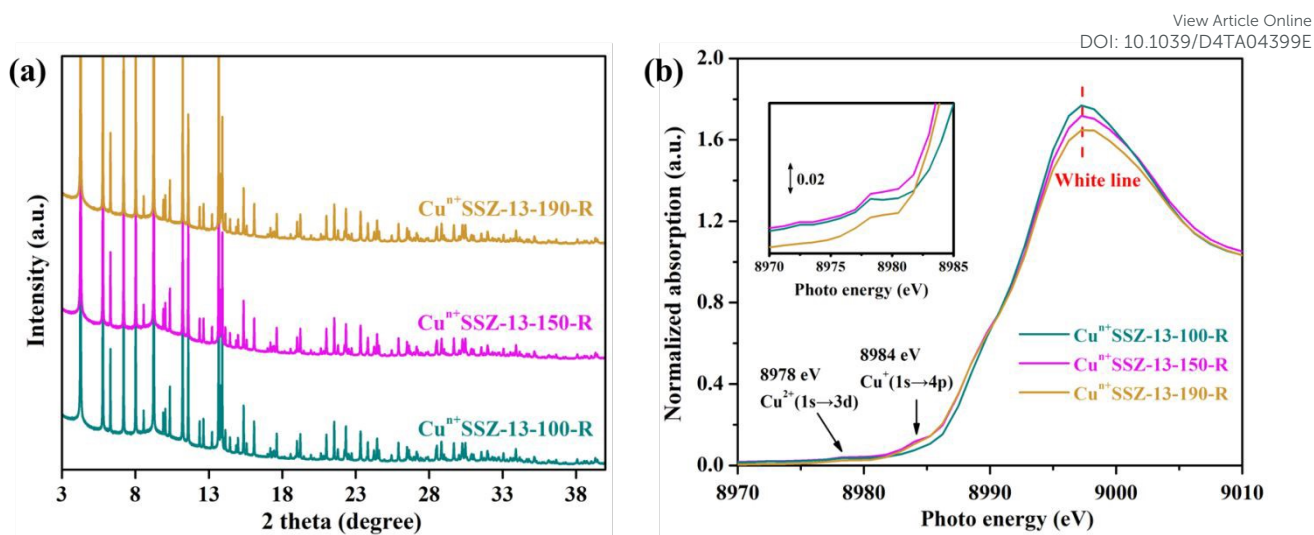


Figure 3. (a) PXRD patterns (wavelength of 0.6880 Å) and (b) Cu K-edge XAS of Cuⁿ⁺SSZ-13 reduced by H₂ at 100, 150, 170 and 190 °C.



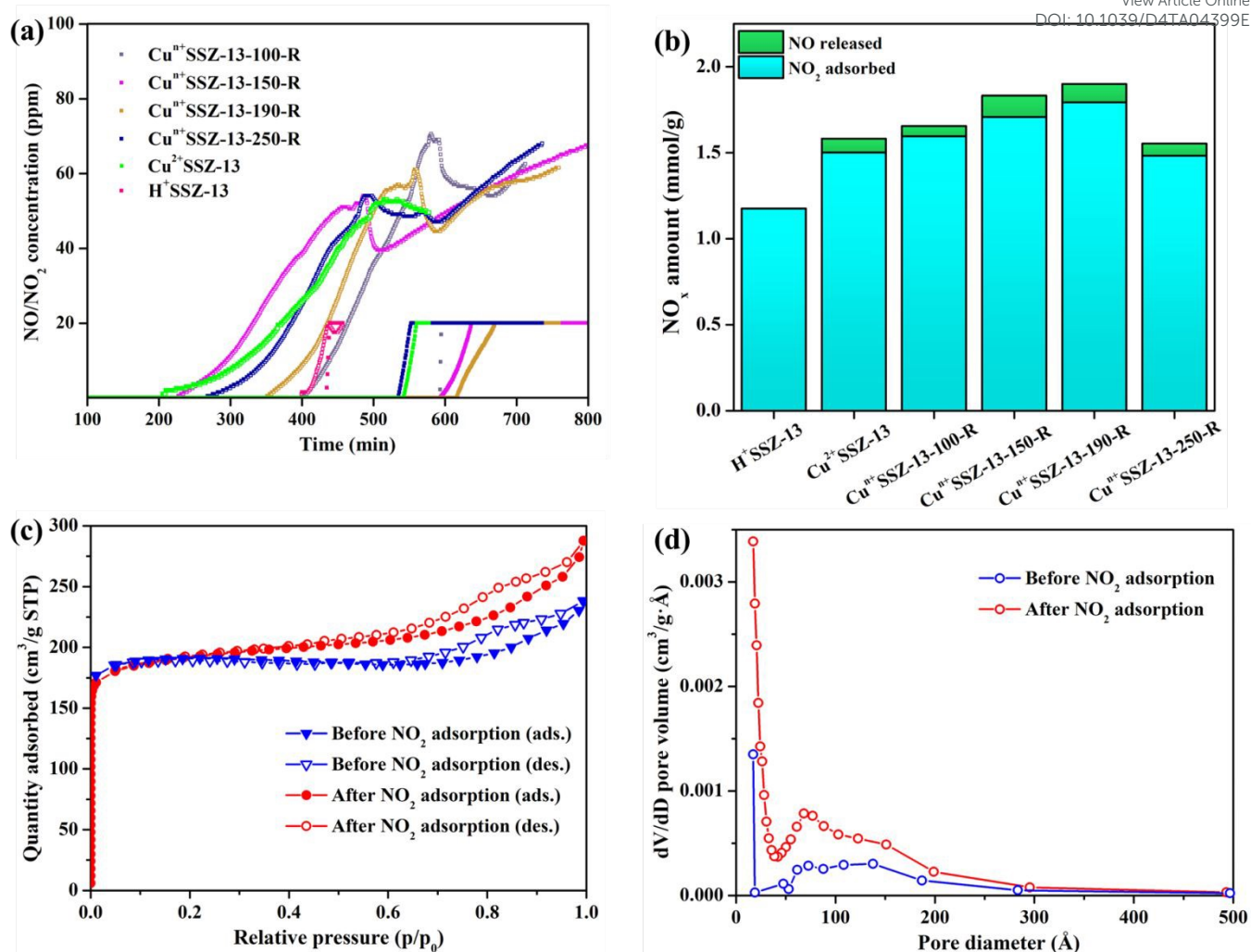


Figure 4. (a) NO₂ (1000 ppm) dynamic column adsorption at room temperature on H⁺SSZ-13, Cu²⁺SSZ-13 and Cu⁺SSZ-13 samples with thermal activation. The hollow (□) and solid (■) dots represent the concentration of NO and NO₂, respectively. (b) The corresponding NO₂ adsorption capacity and NO released amount. (c) N₂ adsorption-desorption isotherms (-196 °C) and (d) pore size distributions of Cu⁺SSZ-13-190-R before and after NO₂ (1000 ppm) dynamic column adsorption.



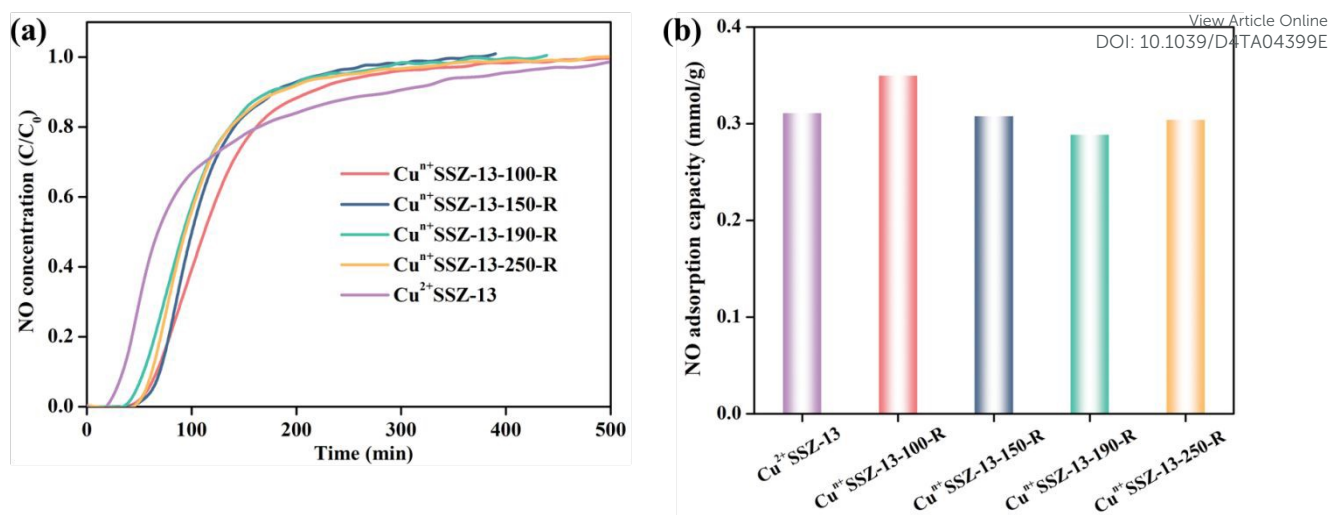
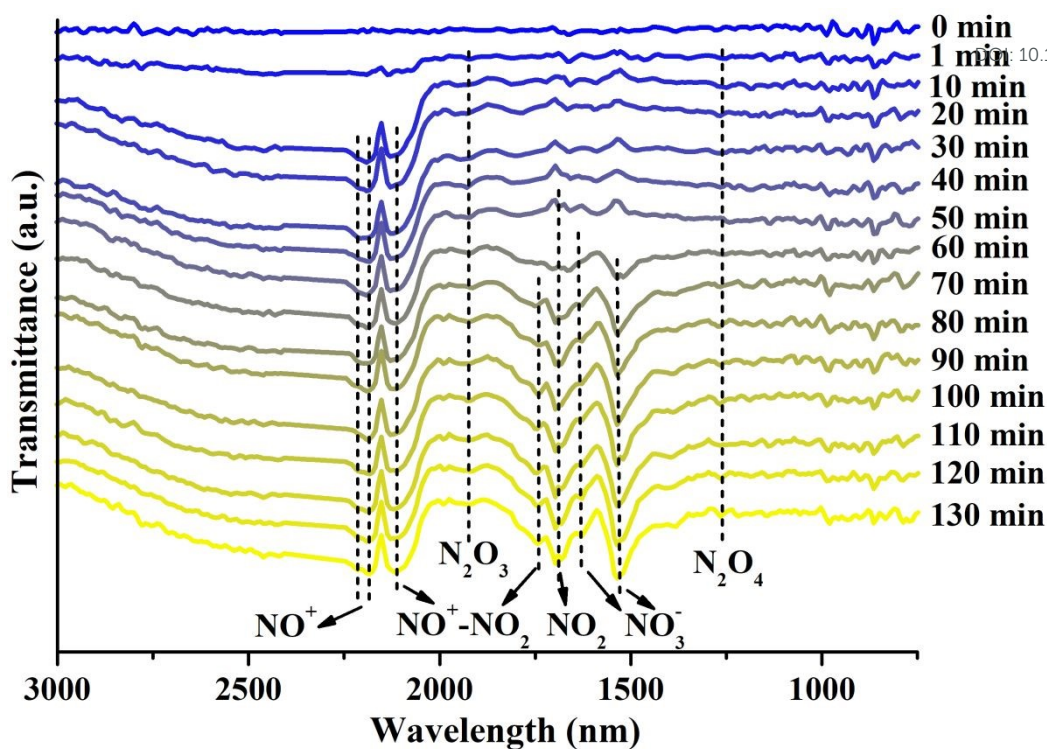


Figure 5. (a) NO (1000 ppm) dynamic adsorption on Cuⁿ⁺SSZ-13 samples at room temperature; and (b) the corresponding NO adsorption capacity.





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Figure 6. In-situ FTIR spectra of Cuⁿ⁺SSZ-13-190-R during NO₂ adsorption, with the background of the fresh sample subtracted (conditions: NO₂ concentration of 1000 ppm, flow rate of 60 mL/min, 25 °C).



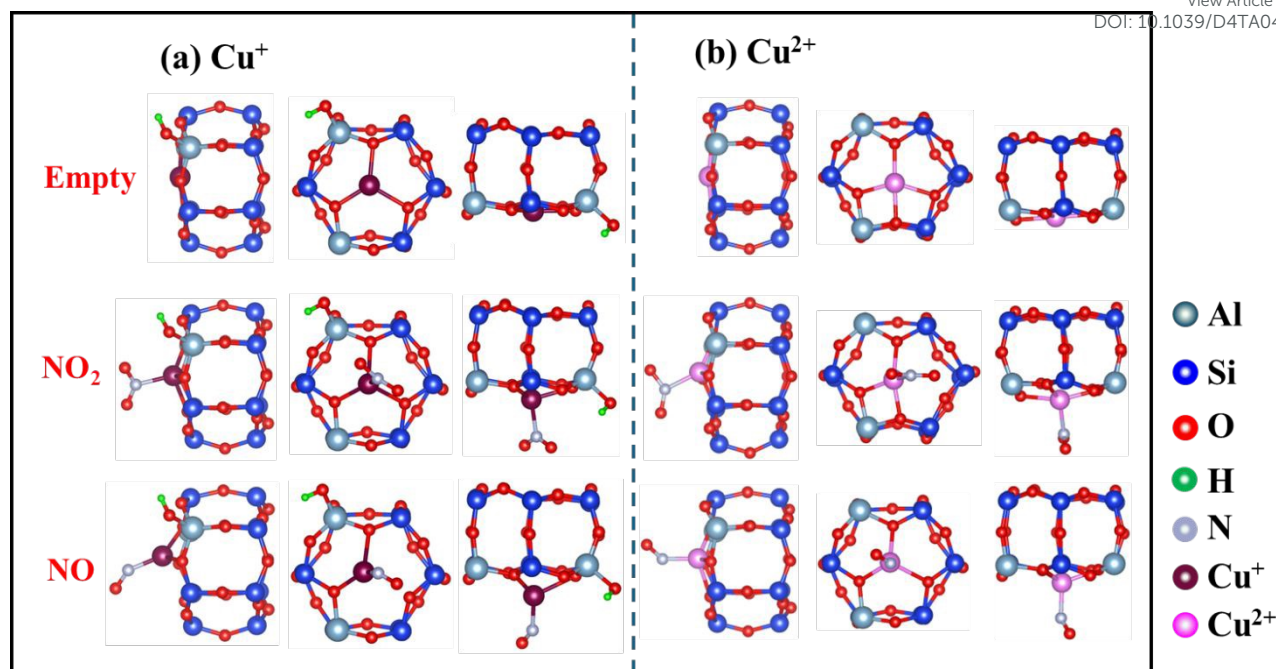


Figure 7. Comparison of optimized local structures of NO_2/NO adsorbed on Cu^+ and Cu^{2+} cations in SSZ-13 zeolite. The top, middle, and bottom images respectively depict the naked cation, and the cation interacting with NO_2 and NO , all located at the 6MR sites.

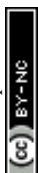


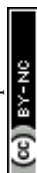
Table 1. The binding energy (kcal/mol) of NO₂ and NO molecules upon adsorption on Cu⁺ and Cu²⁺ in SSZ-13 zeolite calculated by density functional theory (DFT).

	NO ₂	NO
Cu ⁺	-20.06	-30.31
Cu ²⁺	-14.36	-30.78

Table 2. Changes in electron occupancies (ΔO_c) in outer-shell orbitals of N, O and transition metal ions upon NO₂ adsorption (Lowdin). Data was derived from the electron occupancies before and after NO₂ and NO adsorption on Cu⁺SSZ-13 and Cu²⁺SSZ-13 zeolites (Table S3).

	N-2s	N-2pz	N-2px	N-2py	O-2s	O-2pz	O-2px	O-2py	O-2s	O-2pz	O-2px	O-2py	Cu-3dz ²	Cu-3d _{xz}	Cu-3d _{zy}	Cu-3d _{x²-y²}	Cu-3d _{xy}	Cu-4s	Cu-4pz	Cu-4px	Cu-4py	Σ 3d	Σ 4s+4p
Cu ⁺	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NO ₂	0.09	0.32	0.08	0.16	0.01	0.23	0.12	0.12	0.02	0.18	0.08	0.12	-0.37	-0.05	-0.07	0.16	0.00	0.01	0.16	0.01	0.01	0.32	0.17
Cu ⁺	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NO	0.28	0.11	0.05	0.06	0.01	0.10	0.03	0.05	0.00	0.00	0.00	0.00	-0.02	-0.18	-0.16	0.15	-0.06	0.05	0.16	-0.04	-0.01	0.27	0.16
Cu ²⁺	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NO ₂	0.10	0.31	0.09	0.15	0.01	0.21	0.13	0.10	0.02	0.19	0.09	0.14	-0.34	-0.09	-0.06	0.46	0.00	0.01	0.14	0.02	-0.01	0.03	0.15
Cu ²⁺	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NO	0.23	0.04	0.03	0.06	0.02	0.01	0.07	0.06	0.00	0.00	0.00	0.00	-0.17	-0.19	-0.17	0.47	-0.03	0.01	0.19	0.00	-0.01	0.08	0.19

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Data Availability Statement

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The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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