The potential of Cu-SAPO-44 in selective catalytic reduction of NO*x* with NH3

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**Abstract:** Nitrogen oxides (NO*x*) contribute much to acid rain, photochemical smog and the depletion of tropospheric ozone. A novel, small-pore Cu-exchanged chabazite (Cu-CHA) zeolite, Cu-SAPO-44 was first studied for the selective catalytic reduction of NO*x* with ammonia (NH3-SCR), and exhibits excellent activity and N2 selectivity over the wide temperature window from 200-550 ºC. The Cu contents in Cu-SAPO-44 play a determined role in the NH3-SCR reactions. Two kinds of isolated Cu2+ species inside the large cages and in the six-membered rings of the CHA structure were verified as the active sites, which are responsible for low-temperature and high-temperature activity, respectively. Cu-SAPO-44 has shown to be a promising candidate as a SCR catalyst for deNO*x* with great potential in after-treatment systems for either mobile or stationary sources.

Introduction

Nitrogen oxides (NO*x*) contribute much to acid rain, photochemical smog and the depletion of tropospheric ozone. Cu-exchanged zeolites have demonstrated widespread use as catalyst materials in the abatement of NO*x* (deNO*x*), especially from mobile sources.[[1](#_ENREF_1)] Recently, Cu-exchanged small-pore zeolites with chabazite structure (Cu-CHA) have shown to be excellent catalysts in the selective catalytic reduction of NO*x* with NH3 (NH3-SCR).[[2](#_ENREF_6)] The structure of this zeolite offers a unique opportunity to study the nature of active sites, as in contrast to many other zeolites, only isolated Cu2+ ions locating at ion- exchange sites are present in the structure.[[3](#_ENREF_11)]

As a typical Cu-CHA zeolite, Cu-SSZ-13 has been hydrothermally synthesized using N,N,N-trimethyl-1-1-adamantammonium hydroxide (TMAdaOH) as a structure directing agent (SDA), which exhibits extraordinary catalytic properties in NH3-SCR and has been commercialized for NO*x* emission control.[[2a](#_ENREF_6), [2b](#_ENREF_7), [4](#_ENREF_12)] However, the relatively high cost of TMAdaOH hinders wide applications of Cu-SSZ-13. Cu-SSZ-13has also been synthesized by inexpensive copper-amine complex.[[5](#_ENREF_13)] Simultaneously, another Cu-CHA zeolite Cu-SAPO-34, was reported to be a robust NH3-SCR catalyst and can also be synthesized using a relatively low-cost SDA, such as triethylamine, and morpholine.[[2c](#_ENREF_8), [2d](#_ENREF_9), [6](#_ENREF_15)] Unfortunately, the structure destruction of these zeolites and agglomeration of the active phase results in decreased NH3-SCR activity after hydrothermal treatment.[[7](#_ENREF_19)] Hence, the search for high-activity small-pore zeolite continues.

Herein, we report for the first time, insights into the performance and active sites of a novel Cu ion-exchanged SAPO-44 zeolite (Cu-SAPO-44) in NH3-SCR. Cu-SAPO-44 catalyst was prepared by using inexpensive cyclohexylamine as SDA and exhibits excellent activity and N2 selectivity over a wide temperature window even after severe hydrothermal aging. X-ray absorption fine structure (XAFS) confirmed that isolated Cu2+ species with high thermostability are the active sites. This introduces a new opportunity for the potential industrial application of Cu-SAPO-44 and provides a choice for NOx control in diesel exhaust.

Results and Discussion



**Figure 1.** XRD patterns for SAPO-44, Cu0.1-SAPO-44, and Cu0.1-SAPO-44-750.

The XRD pattern of the parent zeolite shows a CHA structure (Figure 1).[[8](#_ENREF_20)] Although it was speculated in the literature that SAPO-44 has a slightly distorted structure and less amount of silica patches compared to that of SAPO-34, which has the same structure as CHA, the IR spectrum of the as-synthesized parent zeolite is completely identical to that of SAPO-44 (Figure S1, Supporting Information).[[8](#_ENREF_20)] Moreover, the template adoped in this work, cyclohexylamine, is indeed a typical template for the crystallization of SAPO-44.[[6b](#_ENREF_16)]

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| **Table 1.** Textural properties and ICP data for SAPO-44 and Cu0.1-SAPO-44. | | | | | | | | |
| Sample | Surface areas  (m2/g) | Pore  size  (nm) | Pore volume  (cm3/g) | ICP data (wt.%) | | | | | |
| Cu | Si | Al | P | Si/(Al+Si+P)  molar ratio |
| SAPO-44 | 565 | 0.47 | 0.14 | ‒ | 7.29 | 19.42 | 16.60 | 0.17 |
| Cu0.1-SAPO-44 | 225 | 0.39 | 0.09 | 1.59 | 7.30 | 19.61 | 16.50 | 0.17 |
|  | | | | | | | | |

As an example of Cu-exchanged SAPO-44, Cu0.1-SAPO-44 experienced a significant drop in crystallinity. Moreover, a “bump” is detected between 15 and 30o demonstrating formation of an amorphous phase upon SAPO-44 hydrolysis during ion-exchange process. However, the diffraction peaks of Cu0.1-SAPO-44 with much lower intensity still agree well with those of SAPO-44, indicating that the crystalline structure of SAPO-44 is essentially unchanged after the Cu ion-exchange process. Although Cu0.1-SAPO-44 shows less crystallinity, its elemental contents (Si, Al and P) are essentially the same as those of the parent zeolite (ICP analysis, Table 1). In fact, the microporous zeolite would undergo the irreversible hydrolysis with different levels during ion-exchange process, thereof the decreased intensity of diffraction peaks was ascribed to dissolution of zeolite during the ion-exchange process.[[2d](#_ENREF_9)] The incorporation of Cu in SAPO-44 was demonsrated by ICP data (Table 1), while no diffraction peaks of copper species (Cu, Cu2O or CuO) were observed in the XRD pattern, suggesting that Cu species are well dispersed in Cu0.1-SAPO-44.[[9](#_ENREF_21)]

The textural properties of SAPO-44 and Cu0.1-SAPO-44 were investigated. As observed in Table 1, Cu0.1-SAPO-44 experienced a significant surface area and pore volume loss after ion-exchange treatment. SEM images of SAPO-44 show cubic-like rhombohedral morphology (Figure S2, Supporting Information), quite similar to those in the literature.[[10](#_ENREF_22)] After Cu ion exchange, the morphology of Cu0.1-SAPO-44 was nearly identical to that of the parent SAPO-44 except for some irregular fragments, in agreement with the decrease of crystallinity as revealed by XRD (Figure 1).

The highest Cu content was observed at Cu0.1-SAPO-44 (Table S1, Supporting Information). As observed in Figure 2a and b, the SCR activity was promoted with the increasing Cu content in Cu*x*-SAPO-44, and Cu0.1-SAPO-44 shows the optimal NO*x* conversion and N2 selectivity with nearly 100% from 200 to 550 oC, indicating more Cu content provides more active species. In the case of Cu0.125-SAPO-44, a slight improvement in the low-temperature activity was accompanied by an evident decrease in high-temperature activity in comparison with Cu0.1-SAPO-44, indicating that the excessive Cu2+ concentration in CuSO4 exchange solution might give rise to the formation and aggregation of CuO*x* species in Cu*x*-SAPO-44.[[11](#_ENREF_23)]



(a)



(b)



(c)

**Figure 2.** (a) NO conversion, (b) N2 selectivity of Cu*x*-SAPO-44 as a function of temperature, and (c) NO conversion with the H2O or/and SO2 at 300 oC for Cu0.1-SAPO-44 as a function of temperature.

Cu0.1-SAPO-44 exhibits comparable activity with Cu/SAPO-34 in literature,[[2d](#_ENREF_9)] which is highly active and selective in NH3-SCR. However, in the present work, Cu0.1-SAPO-44 shows much higher activity than Cu0.1-SAPO-34 especially at high temperatures notwithstanding a relatively high Cu amount in Cu0.1-SAPO-34 (Figure S3a and b, Table S1, Supporting Information). This was probably ascribed to the formation of CuO*x*, which decreased the activity in the high temperature range seriously due to the overoxidation of NH3.[[5b](#_ENREF_14), [9](#_ENREF_21), [12](#_ENREF_25)]

As the composition of diesel exhaust is complicated, the SCR activity of Cu0.1-SAPO-44 were measured in the presence of H2O or/and SO2 at 300 oC (Figure 2c). There is no negative effect on NO*x* conversion when 10% H2O was present in the feed gas. However, NO*x* conversion decreased following the introduction of SO2 (and H2O). Fortunately, the initial activity can be recovered after removing SO2 and heat-treatment at 500 oC. Hence, the commonly encountered SO2 inhibiting effect at lower temperatures for SCR catalysts due to the coverage of active sites by ammonium sulfates and Cu sulfate species could be overcome by periodical exposure to high temperatures during high speed and high load phases or diesel particulate filter (DPF) regeneration.[[1c](#_ENREF_3), [13](#_ENREF_26)]



**Figure 3.** NO conversion and N2 selectivity for Cu0.1-SAPO-44-750 as a function of temperature.

To probe hydrothermal stability, Cu0.1-SAPO-44 was further treated in 10% H2O in air at 750 oC and 800 oC (denoted as Cu0.1-SAPO-44-*T*), respectively. As shown in Figure 3, for Cu0.1-SAPO-44-750, not only was N2 selectivity not affected, but NO*x* conversion also remained at nearly 100% from 200 to 400 oC. Meanwhile, only a slight collapse of the crystal structure was observed, as a consequence of the high framework stability (Figure S2c, Supporting Information). However, a significant deactivation of Cu0.1-SAPO-44 was detected after hydrothermal treated at 800 oC (Figure S4a, Supporting Information), and a broad bump was observed on the XRD pattern of Cu0.1-SAPO-44-800, even through the SAPO-44 phase was maintained. This can be ascribed to the partial collapse of the crystal structure during the high-temperature hydrothermal treatment (Figure S4b, Supporting Information).[[13b](#_ENREF_27)]

NH3-SCR kinetics were further investigated on Cu*x*-SAPO-44 samples at a GHSV of 500,000 h−1. Arrhenius plots in the differential kinetic regime (NO*x* conversion ≤ 15%) are created by calculating SCR reaction rates on per mole of Cu atoms. As displayed in Figure 4, the apparent activation energy (*E*a) of the Cu*x*-SAPO-44 catalyst for the NH3-SCR reactions measured in this temperature regime is ~38.2±1.9 kJ/mol. Compared to the reported apparent *E*a values,[[9](#_ENREF_21), [14](#_ENREF_28)] the apparent *E*a value of the Cu*x*-SAPO-44 catalyst is lower, and is comparable with that of Cu ion-exchanged SAPO-34 catalyst, suggesting its potential industrial application as a SCR catalyst for deNO*x* (Figure S3c, Supporting Information).

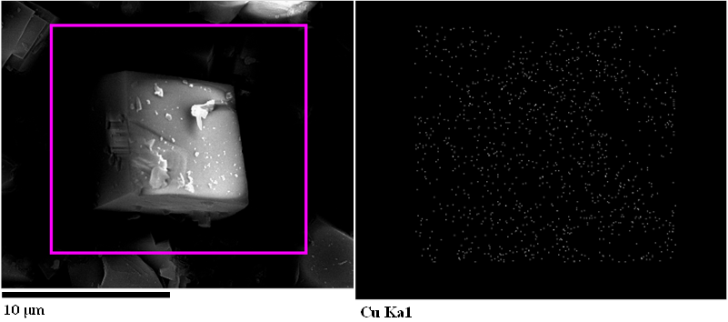


**Figure 4.** Arrhenius plots of the SCR reaction rates over Cu*x*-SAPO-44 catalysts.

In order to clarify the form of Cu species present in Cu*x*-SAPO-44, the Cu 2p3/2 transitions were monitored by XPS (Figure S5, Supporting Information). No peak was detected indicating that the Cu species were not predominantly located at the surface after ion-exchange treatment.[[15](#_ENREF_29)] Evidently, this result is not sufficient to describe the specific state of Cu in bulk zeolite, and several scenarios may be envisaged. In previous studies, several types of copper species, such as isolated Cu2+ and Cu+ ions,[[16](#_ENREF_30)] CuO or Cu2O clusters,[[17](#_ENREF_32)] and dimeric copper species ([Cu–O–Cu]2+),[[18](#_ENREF_34)] have been proposed in Cu-ZSM-5. For Cu-CHA zeolites, isolated Cu ions at the exchange sites were demonstrated to be the active sites for Cu-SAPO-34 and Cu-SSZ-13.[[3](#_ENREF_11), [12](#_ENREF_25)] Is this the same case for Cu-SAPO-44?

According to the EDS elemental mappings, Cu (as well as Si, Al, P and O) was highly dispersed without formation of large bulk structures of Cu-containing species (Figure 5a and b, Figure S6, Supporting Information). Moreover, the apparent aggregated copper species in Cu0.1-SAPO-44 cannot be detected by TEM (Figure S7, Supporting Information).

To analyze in more detail the nature of Cu species, Cu0.1-SAPO-44 was studied by XAFS. Figure 5c shows the XANES spectra of Cu K-edge for Cu0.1-SAPO-44, Cu0.1-SAPO-44-750 and references. The pre-edge feature at 8980 eV with low-intensity, assigning to the dipole forbidden 1*s*→3*d* transition only in Cu2+ complexes, was observed for Cu0.1-SAPO-44, Cu0.1-SAPO-44-750 and CuSO4 (standard sample) (Figure 5c, inset). [[19](#_ENREF_36)] The second pre-edge feature at 8988 eV, assigned to 1*s*→4*pz* transition and associated with a geometric distortion of the tetrahedral Cu (II) site, was present in CuO (standard sample) (Figure 4c, inset), while was absent in others.[[20](#_ENREF_37)] This confirmed the isolated Cu2+ ions in Cu0.1-SAPO-44 and Cu0.1- SAPO-44-750, and the Cu2+ ions are not affected by the hydrothermal treatment.[[1d](#_ENREF_4)] The corresponding Fourier-transformed *k*3-weighted Cu K-edge patterns give more direct evidence (Figure 5d). In the case of CuO, two characteristic peaks at ~2.6 and 3.0 Å were detected, which are attributed to the neighboring copper atoms (Cu-O-Cu) in CuO.[[21](#_ENREF_38)] However, the patterns of Cu0.1-SAPO-44 and Cu0.1-SAPO-44-750 show significant similarities to that of CuSO4. The peak at ~1.5 Å is assigned to Cu-O scattering, confirming the existence of isolated mononuclear Cu2+ species.[[3](#_ENREF_11)]



(c)

(b)

(a)



(d)



**Figure 5.** FESEM image (a) and the corresponding distribution map of Cu (b) for Cu0.1-SAPO-44; (c) normalized Cu K-edge XANES spectra and (d) Fourier-transformed *k3*-weighted Cu K-edge EXAFS functions for Cu0.1-SAPO-44, Cu0.1-SAPO-44-750 and the reference samples.

Combined with the catalytic activity of Cu0.1-SAPO-44 and Cu0.1-SAPO-44-750, the active sites for SCR reactions are proposed as isolated Cu2+ ions within the pores at the exchange sites, which seem to be the most stable locations.[[15](#_ENREF_29)] This result is in accordance with previous results in fact that the high hydrothermal stability of Cu-CHA (Cu-SSZ-13 and Cu-SAPO-34) catalysts is attributed to the preferential coordination of cationic Cu species to the double six-ring cages located in the CHA cavities.[[2b](#_ENREF_7), [4](#_ENREF_12), [22](#_ENREF_39)] According to the results of kinetics measurement (Figure 4), the order of reaction rates for Cu*x*-SAPO-44 is consistent with that of NO*x* conversion, which further verifies the isolated Cu2+ ions are the active sites.[[23](#_ENREF_40)]

Based on the XRD patterns of Cu0.1-SAPO-44-750 and Cu0.1-SAPO-44-800 (Figure 1, and Figure S4a, Supporting Information), no Cu-related phases (Cu, Cu2O, CuO, etc.) were detected, indicating that the Cu2+ ions are stable at the ion-exchanged sites under the severe aging condition. This also demonstrated that the active isolated Cu2+ ions are not incorporated in the SAPO-44 framework but localized in the pores of zeolites.



**Figure 6.** EPR spectra of fresh Cu*x*-SAPO-44 samples recorded at 87 K.



**Figure 7.** H2-TPR profiles for SAPO-44, Cu0.1-SAPO-44 and Cu0.1-SAPO-44-750.

In previous literature, the coordination and positions of these isolated Cu2+ ions from ion exchange can be probed by EPR and H2-TPR.[[2a](#_ENREF_6), [2d](#_ENREF_9), [24](#_ENREF_41)] Figure 6 presents EPR results of the Cu*x*-SAPO-44 samples at 87 K. By analyzing the hyperfine features, g// = 2.394, A// = 136 G, and g⊥= 2.05 are obtained, which are consistent with an octahedral coordination of Cu2+ ions.[[9](#_ENREF_21), [24](#_ENREF_41)] This indicates the isolated Cu2+ ions are octahedrally coordinated and located within the CHA cages of SAPO-44.[[24](#_ENREF_41)]

As shown in Figure 7, no reduction peak was observed for SAPO-44, indicating that H2 consumption for the Cu-containing samples are attributed to the reduction of copper species.[[12](#_ENREF_25)] Cu0.1-SAPO-44 shows two hydrogen reduction peaks at 236 and 320 oC in the test temperature range, which are significantly different from those of Cu0.1-SAPO-34 (Figure S3d, Supporting Information), bus similar with that of Cu-SSZ-600.25 The prior studies demonstrated that these two peaks were arising from Cu2+ reduction with different ionic positions in Cu-CHA zeolite structure.[[13b](#_ENREF_27)] The first copper ions which are more easily reduced occupy sites inside the large cages of the CHA structure, while the next copper ions which are difficult to reduce and require a higher temperature during H2-TPR tests occupy the most stable cationic sites in the six-membered rings.[[25](#_ENREF_42)] For Cu0.1-SAPO-44-750, the first hydrogen reduction peak became larger while the second one was much broader, suggesting that migration of copper ions from the most stable sites to the easily reduced sites have taken place during the high-temperature hydrothermal treatment.[[25c](#_ENREF_44)] This is the reason why NO conversions of Cu0.1-SAPO-44-750 maintained at relative low temperature, meanwhile decreased at high temperatures (> 400 oC) (Figure 3).

Conclusions

Cu ion-exchanged SAPO-44 zeolite, Cu*x*-SAPO-44 has been synthesized using inexpensive cyclohexylamine as template and Cu ion exchange, which exhibits excellent activity and N2 selectivity over the wide temperature window even after severe hydrothermal aging. The Cu contents in Cu-SAPO-44 play a determined role in the NH3-SCR reactions. Two kinds of isolated Cu2+ species inside the large cages and in the six-membered rings of the CHA structure were verified as the active sites, which are responsible for low-temperature and high-temperature activity, respectively. These preliminary results demonstrated that Cu-SAPO-44 could be a potential SCR catalyst in after-treatment systems for either mobile or stationary sources.

Experimental Section

**Sample preparation**

In the preparation of SAPO-44, the gel with molar composition: 3SiO2/4Al2O3/5P2O5/10C6H13N/200H2O was prepared by mixing phosphoric acid (H3PO4, 85 wt.% aqueous solution), pseudo-boehmite (Al2O3, 78 wt.%), colloidal silica sol (40 wt.% suspension in water) and deionized water with vigorous stirring for 40 min at room temperature.[[6a](#_ENREF_15), [6b](#_ENREF_16)] After that, cyclohexylamine template (C6H13N) was added to the resulting viscous gel and then aged with stirring at room temperature over 12 h. The gel obtained was then heated statically for 96 h at 200 oC in a Teflon-lined steel autoclave. The product was recovered by vacuum filtration, washed with deionized water, and dried at 100 oC for 12 h, which was followed by calcination at 550 oC for 6 h in air in order to remove the zeolite framework structure-directing agent. Then, the zeolite samples were ion-exchanged twice in a 1 M solution of NH4NO3 (by suspending 1.0 g of zeolite sample in 46 mL NH4NO3 solution) at 80 oC for 2 h and dried in air at room temperature to generate NH4-SAPO-44 samples.[[26](#_ENREF_45)] The ion-exchanged Cu-SAPO-44 was prepared by mixing 1.0 g of NH4-SAPO-44 with 40 mL of CuSO4 solution. The samples with different Cu loadings were obtained by changing the amount of Cu2+ ions in CuSO4 solution (molar concentration: 0.025 M, 0.05 M, 0.1 M, and 0.125 M). The slurry was continuously stirred at 70 oC for 1 h. The exchanged zeolite was separated using vacuum filtration, dried at 100 oC for 12 h, and further calcined in air at 550 oC for 6 h to remove the residual templates and denoted as Cu*x*-SAPO-44, where “*x*” represents the molar concentration of CuSO4 solution. For comparison, the Cu0.1-SAPO-34 catalyst was prepared using commercial SAPO-34 as parent zeolite, and following the ion-exchanged procedure as above mentioned.

Hydrothermal aging of Cu*x*-SAPO-44 was carried out in a fixed-bed quartz reactor. Cu*x*-SAPO-44 catalysts were heated to 750 oC and 800 oC at a ramp rate of 10 oC/min in a flowing wet-air containing 10% H2O, and held for 12 h and 16 h respectively. The obtained aged samples were denoted as Cu*x*-SAPO-44-*T*, where “*T*” represents the temperature of hydrothermal treatment.

**Characterization**

X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8-FOCUS X-ray diffractometer using Cu Kα radiation at 40 kV and 40 mA. The Brunauer-Emmett-Teller (BET) surface area and pore structure were determined from N2 adsorption/desorption using a Micromeritics ASAP2020M instrument. Before N2 physisorption, the sample was outgassed at 300 oC for 5 h. Inductively coupled plasma-atomic emission spectrometer (ICP-AES) experiments were carried out on the Optima 2100DV instrument from Thermo elemental. Field-emission scanning electron microscopy (FESEM) was performed on a Hitachi SU-70 microscope. Transmission electron microscopy (TEM) equipped with selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS) was conducted on a JEOL JEM-2010 microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data were obtained on an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charging effects, the binding energies were calibrated using the C 1s hydrocarbon peak at 284.8 eV. X-ray absorption fine structure (XAFS) measurements for the Cu K-edge were performed in the transmission mode and fluorescence mode at room temperature on the XAFS station of the 1W1B beamline of Beijing synchrotron radiation facility (BSRF, Beijing, China), respectively. XAFS data were analyzed using IFEFFIT software package.[[27](#_ENREF_46)] Electron paramagnetic resonance spectroscopy (EPR) was used to probe the structural environment of paramagnetic isolated Cu2+ sites. Spectra were recorded at 87 K in vacuum with a Bruker E500 instrument. Temperature-programmed reduction with H2 (H2-TPR) experiments were performed in a quartz reactor with a thermal conductivity detector (TCD) to monitor the H2 consumed. A 50 mg sample was pretreated *in situ* at 500 oC for 1 h in a flow of O2 and then cooled to room temperature in the presence of O2. TPR was conducted at 10 oC/min up to 900 oC in a 30 mL/min flow of 5 vol.% H2 in N2. To quantify the total amount of H2 consumed, CuO was used as a calibration reference.

**Catalytic performance tests**

The steady state NH3-SCR activity over Cu*x*-SAPO-44 catalysts was tested in a fixed-bed quartz tube reactor (6.0 mm i.d.) with a thermocouple placed inside the catalyst bed and in the temperature range 100-550 oC. A model flue gas consisting of 500 ppm NO, 500 ppm NH3, and 5.3 vol.% O2, 10 vol.% H2O (when used), 200 ppm SO2 (when used) and balance, He. The total flow rate was maintained at 300 mL/min, corresponding to a gas hourly space velocity (GHSV) of 100000 h-1. Concentrations of NO and NO2 were monitored by a chemiluminiscence NO*x* analyzer (42*i*-HL, Thermo). N2O and NH3 were detected by quadrupole mass spectrometer (MS, OmniStar 200, Balzers) with a m/z of 44 for N2O, and 17 for NH3. The data for steady-state activity and NO oxidation of catalysts were collected after about 1 h testing.

The reaction kinetics was measured using the analogical condition as the steady-state reaction. Differently, the powder samples were pressed, crushed and sieved (100–200 mesh) prior to use. The GHSV was estimated to be 500000 h−1. The isothermal reactions were conducted at which a stable and small conversion of NO*x* (< 15%) was achieved in an approximate kinetic regime.[[28](#_ENREF_47)] The turnover frequencies (TOF) were estimated by dividing the moles of NO molecules converted per second by the moles of Cu atoms in the catalysts.

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**Keywords:** Nitrogen oxides • Heterogeneous catalysis • Zeolites • EXAFS spectroscopy • Active sites

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