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Effect of the Nature and Location of Copper Species on the Catalytic Nitric Oxide Selective Catalytic Reduction Performance of the Copper/SSZ-13 Zeolite

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The nature and location of copper in Cu/SSZ-13 zeolites synthesized by using a one-pot hydrothermal approach with Cu-tetraethylenepentamine as a template and by the ion exchange of SSZ-13 were investigated by applying H₂-temperature-programmed reduction, FTIR, EPR, and in situ Raman spectroscopic techniques. The one-pot synthesized Cu/SSZ-13 zeolite contains predominantly isolated copper ions in the large cages, whereas copper species in the ion-exchanged Cu/SSZ-13 zeolite occupy sites in the large cages of the chabazite (CHA) structure and the six-membered rings of the CHA structure. If the one-pot synthesized Cu/SSZ-13 zeolite is exchanged with the NH₄NO₃ solution in addition to the removal of a part

of copper ions, the remaining copper ions in the CHA structure relocated from the large cages to the six-membered rings. Isolated copper dominated in all Cu/SSZ-13 zeolites. The in situ Raman spectra demonstrated that Cu–O–Cu dimers form at higher copper content. The bis-μ-oxo dicopper(III) complex is observed only in the ion-exchanged sample upon dehydration. The higher NO selective catalytic reduction activity of the one-pot synthesized sample in a wide temperature range appears to be due to the predominance of isolated Cu²⁺ sites in the large cages, and their higher reactivity is possibly owing to the lower stability of Cu²⁺ at these sites.

Introduction

The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia (NH₃-SCR) is an efficient way for NO_x abatement.^[1–3] Copper-containing zeolites are one of the most active catalyst systems for the related reactions.^[3–8] The most extensive studies have been performed on Cu/ZSM-5 and Cu/BEA zeolites. Cu/BEA demonstrates excellent activity with better hydrothermal stability than does Cu/ZSM-5.^[7,9–11] The ion-exchanged copper-containing SSZ-13 zeolite, based on the small-pore chabazite (CHA) zeolite topology, recently demonstrated higher activity and selectivity to N₂ over a wide temperature range and better hydrothermal stability than did Cu/ZSM-5 and Cu/BEA zeolites.^[12–17]

Typically, the catalytic SCR performance of the copper-containing zeolite greatly depends on the location and nature of

copper species. The existence of various types of copper species in the zeolite has been proposed: Cu²⁺ and Cu⁺ monomers, [Cu–O–Cu]²⁺ dimers, and CuO_x clusters.^[17–19] Isolated Cu²⁺ species are usually postulated as the active sites in the SCR reaction.^[20–22] The preparation method strongly affects the nature and speciation of the copper phase. In general, monomeric copper ions located at the cation-exchange sites dominate in ion-exchanged samples, with the fraction of [Cu–O–Cu]²⁺ dimers typically becoming more important with increasing Cu content.^[18] In contrast, precipitation usually results in the formation of a separate CuO phase located at the external zeolite surface.^[17–19] Lobo et al. suggested that Cu²⁺ ions are located in the six-membered rings of the CHA structure.^[23] Combining extended X-ray absorption fine structure and in situ UV/Vis spectroscopy, Beale et al. proposed that isolated mononuclear Cu²⁺ species slightly shifted toward the edge of the six-membered rings.^[20] Kwak et al. reported that the location of copper species depends on the copper content if the ion-exchange method is used to prepare the Cu/SSZ-13 zeolite.^[15] Copper ions prefer to occupy sites in the six-membered rings over those in the large cages of the CHA structure.^[15] A copper complex was used recently in the synthesis of Cu/SSZ-13, which has the dual function of acting as the template for SSZ-13 formation as well as loading copper at specific locations in the zeolite micropores. The method using the Cu²⁺–tetraethylenepentamine (Cu–TEPA) complex for the one-pot synthesis of the Cu/SSZ-13 zeolite was first reported by Xiao et al.^[24] The resulting Cu/SSZ-13 materials demonstrate high activity in the SCR of NO over a wide temperature range.^[24,25]

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Corma et al. also described the one-pot synthesis of the Cu/SSZ-13 zeolite with a combination of templates (Cu-TEPA and *N,N,N*-trimethyl-1-adamantammonium hydroxide). The material used by Corma et al. was highly active and stable for the SCR of NO_x, even under severe reaction conditions.^[26,27] The same group has also described the one-pot synthesis of the Cu/SAPO-34 zeolite with a combination of inexpensive templates (Cu-TEPA and diethylamine).^[28] One expects that Cu/SSZ-13 prepared by using this method will have more uniformly speciated copper species than comparatively less active zeolites prepared by using conventional methods. So far, however, the location and nature of copper species in one-pot synthesized and ion-exchanged Cu/SSZ-13 zeolites have not been investigated in detail.

Herein, Cu/SSZ-13 zeolites were prepared by using one-pot and ion-exchange methods and characterized by applying H₂-temperature-programmed reduction (H₂-TPR), IR, EPR, and Raman spectroscopy techniques to study the location and nature of copper species. Our study demonstrates that 1) the copper ions in the one-pot synthesized sample are more uniformly speciated as highly dispersed isolated ions in the large cages of the SSZ-13 micropores. In contrast, copper ions in the ion-exchanged sample occupy sites in the small six-membered rings and the large cages of the CHA structure; 2) if the one-pot synthesized sample is treated with NH₄NO₃, a part of copper ions are exchanged by ammonium ions and the remaining copper ions migrate from the large cages to the more stable location in the six-membered rings; and 3) monomeric copper ions dominate in all samples and more dimeric Cu–O–Cu species are present in samples with higher copper content. Meanwhile, the bis-μ-oxo dicopper(III) complex is observed only in the ion-exchanged Cu/SSZ-13 zeolite. The high catalytic activity in the SCR of NO appears to be related to isolated copper ions located in the large cages of the SSZ-13 structure.

Results and Discussion

The elemental composition of Cu/SSZ-13 zeolites as determined by inductively coupled plasma optical emission spectrometry (ICP–OES) analysis is listed in Table 1. The copper loading did not result in a change in the Si/Al content of the parent SSZ-13 zeolite. The one-pot synthesized sample had a similar Si/Al ratio and Cu/Al ratio as did the ion-exchanged zeolite. The subsequent treatment with NH₄NO₃ solutions did not affect the Si/Al ratio but led to a gradual decrease in the

Cu/Al ratio with an increase in NH₄NO₃ concentration. The XRD patterns demonstrate that Cu/SSZ-13 zeolites synthesized by ion exchange (IE-0.36: ion-exchanged sample with Cu/Al = 0.36) and by one-pot synthesis (OP-0.37: one-pot synthesized sample with Cu/Al = 0.37) are highly crystalline and demonstrate the CHA structure (Figure S1, traces a and b). Notably, CuO cannot be observed in the XRD patterns of these samples, which is an indication of the high dispersion of the copper phase.

The H₂-TPR curves used to investigate the reducibility of intrazeolitic copper species in the Cu/SSZ-13 zeolite are shown in Figure 1. For the ion-exchanged sample (IE-0.36), a strong

Figure 1. H₂-TPR profiles of all Cu/SSZ-13 zeolites: a) IE-0.36, b) OP-0.37, c) OP-0.26, d) OP-0.09, and e) OP-0.04.

reduction feature at 240 °C with a shoulder at 400 °C is observed (Figure 1a), which was attributed to the reduction of isolated Cu²⁺ to Cu⁺ at different cation positions in the zeolite structure.^[15] The lower reduction feature arises from the relatively easy reduction of Cu²⁺ located in the large cages of the CHA structure, whereas the higher temperature feature arises from the reduction of Cu²⁺ in the six-membered rings. The one-pot synthesized sample (OP-0.37) demonstrates only a single H₂-TPR reduction feature at 240 °C (Figure 1b). Thus, Cu²⁺ ions are predominantly located in the large cages of the CHA structure in this sample.

To elucidate the origin of this difference between the two Cu/SSZ-13 zeolites, the OP-0.37 sample was ion exchanged with a series of NH₄NO₃ solutions of increasing concentration. The reducibility of copper species in the resulting zeolites was studied by using H₂-TPR. With the increase in NH₄NO₃ concentration, the copper content in Cu/SSZ-13 zeolites decreased gradually (Table 1). Meanwhile, the reduction feature at 240 °C decreased concomitant with the appearance of a new feature at 400 °C (Figure 1c and d). This result indicates that some of the remaining Cu²⁺ ions relocate from positions in the large cages of the CHA structure to cation-exchange positions in the six-membered rings during the ion-exchange process with the NH₄NO₃ solution. With use of a more concentrated NH₄NO₃ so-

Table 1. Elemental composition of Cu/SSZ-13 zeolites as determined from ICP–OES analysis.			
Sample	NH ₄ NO ₃ concentration [M]	Si/Al	Cu/Al
IE-0.36	–	4.3	0.357
OP-0.37	–	4.3	0.365
OP-0.26	0.01	4.3	0.259
OP-0.09	0.025	4.3	0.090
OP-0.04	0.05	4.3	0.036

lution, only the reduction feature at 400 °C was observed (Figure 1e). This tendency is consistent with the known higher stability of Cu^{2+} in the small rings.^[15] During one-pot synthesis, Cu^{2+} ions are chelated by amine complexes and are thus too large to be present in the six-membered rings.^[24,25] However, during ion exchange, Cu^{2+} ions prefer to locate in their more stable positions.

In addition to these features in the H_2 -TPR profiles, there are reduction peaks located at 580 and 535 °C for IE-0.36 and OP-0.37 samples, respectively. These relatively higher temperature reduction peaks are attributed to the reduction of copper dimers from Cu^+ to Cu^0 and to the reduction from Cu^+ monomers to Cu^0 , which occurs only at high temperatures with the collapse of the CHA structure.^[13] Thus, it is reasonable to propose the formation of copper dimers in these samples.

The FTIR spectroscopy of adsorbed CO was performed to study the chemical state of copper sites and their environment in the zeolite.^[15,16] The pretreatment process results in the autoreduction of Cu^{2+} ions in the zeolite. The IR spectra of CO adsorbed on the Cu/SSZ-13 zeolite as a function of CO coverage are shown in Figure 2. The IR spectrum of the IE-0.36 sample (Figure 2a) demonstrates two distinct absorption bands centered at 2145 and 2155 cm^{-1} and labeled as LF (low-frequency) and HF (high-frequency) bands, respectively. These two bands relate to CO coordinated to Cu^+ sites in the six-membered rings (LF) and large cages of the CHA structure (HF).^[16] With the increase in CO coverage, the sites associated with the LF band become saturated with CO whereas the sites in the large cages of the CHA structure are still getting populated. Meanwhile, a new band located at 2180 cm^{-1} appeared

and its intensity became stronger with the increase in CO coverage. This band was assigned to dicarbonyl species bounded to Cu^+ .^[16] The IR spectrum of the OP-0.37 sample demonstrates only one absorption band at 2155 cm^{-1} (Figure 2b), irrespective of the CO coverage. Consistent with the TPR results, the FTIR results demonstrate that all copper ions are located in the large cages of the CHA structure in the one-pot synthesized Cu/SSZ-13 zeolite. As expected, if OP-0.37 was ion exchanged with NH_4NO_3 , the IR spectra of these samples demonstrate two distinct absorption bands centered at 2145 and 2155 cm^{-1} (Figure 2c–e). This result indicates that the remaining Cu^{2+} ions in the CHA structure relocated during ion exchange.

Figure 3. EPR spectra of Cu/SSZ-13 zeolites measured at 100 K: a) IE-0.36, b) OP-0.37, c) OP-0.26, d) OP-0.09, and e) OP-0.04.

Figure 2. FTIR spectra of CO adsorbed on Cu/SSZ-13 zeolites: a) IE-0.36, b) OP-0.37, c) OP-0.26, d) OP-0.09, and e) OP-0.04. The dotted arrow indicates an increase in the gas phase equilibrium pressure of CO.

The EPR spectra of Cu-SSZ-13 zeolites were recorded at 100 K, in which the characteristic copper hyperfine structure can be resolved. The characteristic structure of Cu^{2+} complexes is shown in Figure 3, which results from hyperfine coupling between the 3d unpaired electron and the copper ($I=3/2$) nuclear spin.^[25] The spectral features agree well with the isolated octahedral copper complexes observed in zeolites, in which the surrounding ligands are water or hydroxyl groups.^[16,29,30] This result implies that all the Cu-SSZ-13 samples contain predominantly isolated copper species, which is in accordance with the work of Lamberti et al.^[31] On the basis of the results of extended X-ray absorption fine structure and UV/Vis spectroscopy, Beale et al. proposed that isolated Cu^{2+} is the active site for the NH_3 -SCR reaction.^[20–22] The EPR spectra of OP-0.37 and IE-0.36 samples demonstrate the same features (Figure 3a and b). If the OP-0.37 sample is ion exchanged with the NH_4NO_3 solution, the copper content decreases (Table 1). The EPR signal intensity becomes stronger with the increase in copper content (Figure 3). Meanwhile, the peak width increases, which stems from the dipole–dipole interactions between Cu^{2+} ions. This finding demonstrates that the distance between Cu^{2+} ions becomes

shorter as the copper loading increases, which in turn indicates that the formation of copper dimers is highly possible in the samples with high copper loadings.

Furthermore, the overall intensity of the EPR spectra decreased significantly if the samples were dehydrated before the measurement because Cu^{2+} species are autoreduced to Cu^+ species. This explanation was discarded earlier by Lamberti et al.^[31] These authors put forward, as the most reasonable explanation, that the loss of EPR intensity is due to a change in the coordination environment (water is removed, and the interaction of Cu^{2+} ions with the oxygen anions of the zeolite increase). We refer to the work of Lamberti et al for relevant explanations for the change in the EPR spectra.

The in situ Raman spectra were collected for high-temperature calcined Cu/SSZ-13 zeolites (Figure 4). All samples demonstrate the characteristic Raman band of the CHA structure at 475 cm^{-1} . In addition, the Raman spectra of the IE-0.36 and

Figure 4. In situ Raman spectra of Cu/SSZ-13 zeolites: a) IE-0.36, b) OP-0.37, c) OP-0.26, d) OP-0.09, and e) OP-0.04.

OP-0.37 samples demonstrate an intense Raman band at 350 cm^{-1} and two weak bands at 425 and 535 cm^{-1} (Figure 4a and b). These bands relate to Cu–O–Cu vibrations, which generally fall in the $350\text{--}600\text{ cm}^{-1}$ region.^[18] Notably, the use of laser excitation at 325 and 266 nm did not give rise to these bands in the Raman spectra, which confirms that these vibrations are in resonance with the electronic transition. Schoonheydt et al. reported that the vibrational frequency of Cu–O–Cu species is highly dependent on the Cu–O–Cu angle. In the Cu/ZSM-5 zeolite, this angle is approximately 140° .^[18] We performed DFT calculations to correlate the Raman shift to the Cu–O–Cu angle for a model representing Cu/SSZ-13 zeolite (Figure S2). Our calculation suggests that the Cu–O–Cu symmetric stretching frequency at 361 cm^{-1} corresponds to a Cu–O–Cu angle of 160° , which is in good agreement with the experimental data (350 cm^{-1} ; Figure 4a and b). The occurrence of Cu–O–Cu species for these samples is consistent with their high copper loadings. Compared with the OP-0.37 sample, the Raman band arising from Cu–O–Cu species greatly weakened

in intensity (I_{350}/I_{475}) with the decrease in the Cu/Al ratio in the Cu/SSZ-13 zeolite to 0.26 (Figure 4b and c). The absence of a band at 350 cm^{-1} in the Raman spectra of OP-0.09 and OP-0.04 samples confirms that these samples do not contain Cu–O–Cu species (Figure 4d and e).

Interestingly, an additional Raman band at 610 cm^{-1} is observed exclusively in the spectrum of the IE-0.36 sample (Figure 4a). This copper-related Raman band has been assigned to a bis- μ -oxo dicopper(III) complex.^[32] This assignment is supported by DFT calculations (591 cm^{-1} ; Figure S3). The Cu–O–Cu angle of 110° matches well with the predictions by the Schoonheydt group.^[18] This result confirms that the speciation of copper in the one-pot synthesized sample is more uniform than in the ion-exchanged sample.

The NO conversion over Cu/SSZ-13 zeolites is plotted in Figure 5 as a function of the reaction temperature in the temperature range $150\text{--}500^\circ\text{C}$. Cu/SSZ-13 zeolites with low copper

Figure 5. NO conversion profile of Cu/SSZ-13 at various temperatures in a gas mixture containing 1000 ppm of NO, 1000 ppm of NH_3 , and 5% of O_2 with balance of He.

content demonstrated low activities than did catalysts with high copper content, which is mainly due to the lower density of active sites of the lesser active materials. The OP-0.37 and OP-0.26 samples maintain their high conversion ($>90\%$) up to 500°C , whereas the NO conversion of the IE-0.36 sample decreased above 400°C . This difference in performance at high temperature is consistent with the work of Xiao et al., who were the first to report the one-pot synthesis of the Cu/SSZ-13 zeolite.^[24,25] The NO reduction activity was suppressed at high temperatures if the ion-exchanged Cu/SSZ-13 zeolite with high copper content was used for the SCR of NO_x .^[14] The copper loading in the OP-0.37 and IE-0.36 samples are the same (Table 1). Although the isolated copper ions dominate in both samples as demonstrated by the EPR spectra, the distribution of copper ions and their nature after dehydration are different, as confirmed from TPR, CO IR, and Raman spectroscopy. Copper species in the OP-0.37 sample are more uniform and mainly consist of isolated cations located in the large cages of the zeolite micropore space, whereas copper species in the IE-

0.36 sample are present in the large cages as well as the six-membered rings of the CHA structure. In addition, the dehydrated samples contain Cu–O–Cu dimers. Meanwhile, the bis- μ -oxo dicopper(III) complex is found only in the IE-0.36 sample. Thus, we conclude that the homogeneous speciation of copper in the form of isolated ions in the large cages of the one-pot synthesized Cu/SSZ-13 zeolite accounts for its high NO SCR activity in a wide temperature range. The higher activity of Cu^{2+} ions in the large cages could be related to their lower binding energy to the zeolite lattice compared with Cu^{2+} ions located in the smaller coordination environment of the six-membered rings.

Conclusions

H_2 -temperature-programmed reduction, CO IR, EPR, and Raman spectroscopy techniques were used to study the nature and location of copper species in Cu/SSZ-13 zeolites synthesized by using a one-pot hydrothermal approach with Cu-tetraethylenepentamine as a template and by ion exchange of SSZ-13. The copper ions in the ion-exchanged sample occupy sites in the six-membered rings and the large cages of the chabazite structure, whereas they occupy only the latter sites in the one-pot synthesized sample. Dimeric Cu–O–Cu species were observed in both samples after dehydration, and the bis- μ -oxo dicopper(III) complex is present exclusively in the ion-exchanged sample. The higher activity in a wide temperature range of the one-pot synthesized sample appears to be due to the predominance of isolated Cu^{2+} sites in the large cages, and their higher reactivity is possibly owing to the lower stability of Cu^{2+} at these sites.

Experimental Section

Catalyst preparation

Cu/SSZ-13 was prepared by using a one-pot method according to the literature.^[24,25] Briefly, NaAlO_2 (0.514 g) and NaOH (0.38 g) were dissolved in H_2O . Then, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1.149 g) was added to this solution, followed by the addition of TEPA (1.07 g); the mixture was stirred continuously for 1 h. Silica sol (3.6 mL, 31.5 wt %) was added to the above gel under vigorous stirring. After stirring for 2 h, the final gel was transferred to a Teflon-lined stainless steel autoclave and heated at 140°C for 6 days. The product was collected through filtration, washed with deionized H_2O , and dried at 110°C overnight. To remove the copper that did not coordinate with TEPA in the as-synthesized Cu/SSZ-13 zeolite, ion exchange with the NH_4NO_3 solution was performed before calcination: for this purpose, Cu/SSZ-13 (1 g) was ion exchanged with the NH_4NO_3 solution (100 mL, 1 M) at 80°C for 12 h. After washing with deionized H_2O and drying at 110°C overnight, the product obtained was calcined at 550°C for 8 h in static air. This sample was labeled OP-0.37, with the suffix indicating the Cu/Al ratio. The copper content in the one-pot synthesized Cu/SSZ-13 zeolite was adjusted by ion exchange with solutions of increasing NH_4NO_3 concentration. In a typical exchange experiment, the calcined Cu/SSZ-13 zeolite (1 g) was ion exchanged with NH_4NO_3 (0.08 g) in H_2O (100 mL) at RT for 5 h. After washing with deionized H_2O and drying at 110°C overnight, the product was calcined at 550°C for 4 h in static air. These samples were labeled OP- x , with x indicating the final Cu/Al ratio.

For comparison, a Cu/SSZ-13 zeolite was obtained through ion exchange of H-SSZ-13 with a $\text{Cu}(\text{NO}_3)_2$ solution followed by calcination at 550°C for 4 h in static air. This sample was labeled IE-0.36, with the suffix indicating the Cu/Al ratio.

Catalyst characterization

The XRD patterns were recorded on a Rigaku Miniflex X-ray diffractometer at RT with a $\text{CuK}\alpha$ monochromatic radiation ($\lambda = 1.5418 \text{ \AA}$). The elemental composition of the Cu/SSZ-13 samples was determined from ICP–OES analysis (SPECTRO CIROS CCD ICP–OES with axial plasma viewing). TPR experiments were performed with a flow apparatus equipped with a fixed-bed reactor, a computer-controlled oven, and a thermal conductivity detector. Typically, an amount of the catalyst was contained between two quartz wool plugs in a quartz reactor. Before TPR, the catalyst was oxidized by exposure to a flowing mixture of O_2 (4 vol %) in He at 300°C (heating rate: $10^\circ\text{C min}^{-1}$). After the sample was cooled to RT in flowing N_2 , the sample was reduced in H_2 (4 vol %) in N_2 at a flow rate of 8 mL min^{-1} while heating from RT to 800°C at a ramp rate of $10^\circ\text{C min}^{-1}$.

The FTIR spectra of CO adsorbed to the zeolite samples were recorded in the range of $4000\text{--}400 \text{ cm}^{-1}$ with a Bruker Vertex V70v instrument. The spectra were acquired at a 2 cm^{-1} resolution and averaged over 20 scans. The samples were prepared as thin self-supporting wafers of $5\text{--}10 \text{ mg cm}^{-2}$ and placed inside a controlled environment IR transmission cell, which could heat and cool, gas dose, and evacuate. Before CO adsorption, the catalyst wafer was heated to 550°C at a rate of 2°C min^{-1} . Subsequently, the cell was outgassed at the final temperature until the residual pressure was below 5 mPa. CO was introduced into the sample cell via a sample loop connected to a Valco six-port valve.

The EPR spectra were recorded on a Bruker EPR A200 spectrometer. The samples (10 mg) were introduced into the homemade quartz cup inside the microwave cavity. The EPR spectrometer settings were as follows: center field 3350 G; sweep width 200 G; microwave frequency 9.41 GHz; modulation frequency 100 kHz; power 10.00 mW.

The Raman spectra were obtained on a homemade Raman spectrometer with a triple-stage spectrograph at a resolution of 2 cm^{-1} . The excitation laser line at 532 nm from a semiconductor laser was used as an excitation source. The power of the laser on the sample was approximately 3 mW. The scattered photons were collected in the back-scattering mode. The sample was pressed into self-supporting wafers and placed in an *in situ* quartz cell, equipped with gas inlet/outlet ports and a heater. Then, the samples were pre-treated at 450°C in flowing O_2 for 4 h. The Raman spectrum was recorded after the cell was cooled to RT.

DFT calculations

All the DFT calculations were performed by using Gaussian 09 with the B3LYP hybrid exchange–correlation functional.^[33–36] The 6-311G(d) basis set was used for all atoms. The initial cluster was cut from the crystal structure. All dangling boundary bonds were saturated by H atoms for which the direction was constrained according to the next silicon position. At the first step, all other atoms were fixed while only H bond lengths were optimized. Then, the other atoms were optimized while the H atoms were fixed. All the frequencies obtained by using DFT calculations were compared directly with the experimental data without further correction.

Catalytic activity measurements

The NH_3 -SCR reaction was performed in a parallel 10-flow micro-reactor system with gas mixtures containing NO (0.1 vol%), NH_3 (0.1 vol%), and O_2 (5 vol%) with a balance of He. An amount of the catalyst (10 mg) was diluted with SiC (300 mg) and contained between two quartz wool plugs in a quartz reactor with an internal diameter of 4 mm. The total flow rate per channel was 50 mL min^{-1} . The temperature was varied from 150 to 500°C . The reaction rate was measured during heating of the catalyst beds at a rate of 5°C min^{-1} . Pretreatment involved heating the catalyst samples to 450°C overnight at a rate of 1°C min^{-1} under a He flow at a flow rate of 50 mL min^{-1} . For analysis, the effluent gas was analyzed with a Balzers QMS-200 Omnistar mass spectrometer.

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Keywords: copper • Raman spectroscopy • SCR reaction • SSZ-13 • zeolites

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