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Selective Catalytic Reduction of NO with NH₃ on Cu-SSZ-13: Deciphering the Low and High-temperature Rate-limiting Steps by Transient XAS Experiments

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Abstract: Cu-exchanged small-pore SSZ-13 catalysts have found wide use for the selective catalytic reduction (SCR) of nitrogen oxides from automotive exhaust gases. The transient working environment of the Cu-SSZ-13 catalyst during NH₃-SCR requires studying the rate limiting steps under the different operation conditions this catalyst is exposed to. By exploiting time-resolved operando X-ray absorption spectroscopy in combination with multivariate analysis we followed the transient speciation of Cu during unsteady state conditions. The results reveal that depending on operating temperature two different rate limiting behaviours inhibit the reduction of NO. At temperatures below 283 °C, ammonia hinders reoxidation of solvated Cu^I species thereby inhibiting reduction of NO. Whilst at temperatures of 283 °C and above, the reduction of zeolite bound Cu^{II}(OH) is the rate limiting step in the SCR reaction. The results also reveal the presence of two detrimental side reactions occurring, the direct oxidation of zeolite bound Cu^I at low temperatures and the oxidation of ammonia over Cu at temperatures in excess of 283 °C. Between 250 °C and 350 °C, both side reactions may be present and could explain the dip in the SCR activity typically denoted by the seagull shape.

Introduction

Heterogeneous catalysts for the after-treatment of exhaust gases operate in highly dynamic conditions where, for example, the temperature and gas mixture constantly change. However, only few spectroscopic studies aiming at rationalizing the underlying reaction mechanisms have been conducted under such dynamic conditions. Owing to the development of time-resolved operando methods such as X-ray absorption spectroscopy (XAS), the study of catalysts under the dynamic conditions at which they operate is now possible^[1–5]. The selective catalytic reduction (SCR) of NO_x using small pore size and low metal-loaded Cu-SSZ-13 is such a reaction that takes place under dynamic conditions and has

gained significant attention recently due to the high low-temperature conversion rate of nitrogen oxides in the presence of NH₃^[6–21]. The SCR reaction proceeds according to equation 1.

The SCR reaction scheme is outlined in Figure 1, displaying the mechanism of standard SCR as proposed by Janssens et al.^[15] In this scheme, solvated Cu^{II} nitrates are formed through the oxidation of zeolite-bound Cu^I sites with NO and O₂. Subsequently, the reaction of the nitrates with NH₃ results in the formation of a square-planar Cu^{II} species which decomposes to produce N₂, H₂O and Cu^{II}(OH) sites bound to the zeolite framework. The completion of the cycle is mediated by the reduction of Cu^{II} bound to the zeolite framework to Cu^I through the addition of NH₃ and NO to form intermediate solvated Cu^I species.

Figure 1 Proposed reaction scheme for the standard SCR of NO by NH₃, adapted from Janssens et al.^[15]. The colour assignments of species denote the spectral components observed in time-resolved XAS measurements at each step in the reaction scheme for the standard SCR mode in the work of Marberger et al.^[8]. Green indicates the additional Cu^I-Z species observed through MCR analysis in this work.

Whilst initial studies suggested Cu^I and Cu^{II} cations were occupying sites in the 6-member ring^[22–24], numerous studies

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have since identified that under SCR conditions the Cu^I and Cu^{II} ions can be solvated into the pores of the SSZ-13 structure^[8,9,21,25,26]. Recent work following the auto-reduction of Cu loaded chabazite systems by Martini et al^[21] has elucidated the structure of the Cu^I and Cu^{II} framework zeolite sites using chemometrics. These data suggested the presence of Cu within both the 6-member and 8-member rings of the zeolite at temperatures above approximately 150 °C. In particular, through auto-reduction in He the dominant stable states are proposed to be isolated Cu^I ions within the 6-member ring and hydrated Cu^{II} sites bound to the zeolite framework within the 8-member ring as proposed by Janssens et al^[15].

Elsewhere the low temperature standard SCR mechanism has been proposed to proceed via solvated species^[19]. The activation of oxygen over linearly solvated NH₃ Cu^I species has been proposed as being a key intermediate to the formation of square planar solvated Cu^{II} species. In another proposed mechanism both the interaction with the zeolite framework and the role of solvated species are required for the complete standard SCR reaction^[27]. However, all proposed mechanisms propose the presence of linear solvated species and of square planar Cu species, and for a cycling in the Cu oxidation state to occur. Therefore, XAS studies can provide significant insight into standard SCR mechanism through probing the Cu oxidation state and coordination geometry.

In our recent work^[8], the transient occurrence of a solvated square planar Cu^{II} species after NH₃ is removed from the gas feed concurrent with a temporary higher NO conversion demonstrated the inhibiting effect of NH₃ on the reoxidation of Cu^I in the low-temperature regime. Furthermore, the increase in conversion of NO with increasing temperature was shown to correlate with the loss of NH₃-solvated Cu complexes and related to an increase in Cu ions bound to the zeolite framework. However, the distinction between Cu^I and Cu^{II} bound zeolite states during SCR was not possible in linear combination analysis of the Cu K-edge XAS experiments due to the problem of preparing appropriate reference compounds representing these species. While the studies to date have provided significant insight into the reaction scheme for the standard SCR of NO, further insight into the dynamic Cu speciation under operando SCR conditions is achieved here through re-analysis of our previously published results^[8] together with new experiments at higher temperatures and without the presence of water in the feed. In this work multivariate analysis methods^[21] have been employed to determine the dynamic Cu speciation during transient NH₃ and NO removal and addition experiments, thereby revealing new insights in the low temperature and high temperature rate limiting steps.

Results and Discussion

Typically, linear combination fitting of XAS spectra is achieved using reference compounds allowing for interpretation of the present species within a reaction mixture. Normalised experimental XANES (X-ray absorption near edge structure)

spectra, $\mu^{\text{exp}}(t, E)$, can accurately be described by a linear combination of pure spectral components (individual spectra that can be assigned to a particular species), $\mu_i^{\text{pure}}(E)$, where $\omega_i^{\text{pure}}(t)$ gives the time dependent concentration weighting during a time-resolved operando XAS experiment:

$$\mu^{\text{exp}}(t, E) = \sum_i^{N_{\text{pure}}} \omega_i^{\text{pure}}(t) \mu_i^{\text{pure}}(E) \quad (2)$$

It has been well established that at low temperature under exposure of NH₃ Cu is solvated from the zeolite structure into the pore. In such circumstances the use of molecular complexes accurately represents the coordination environment present in the system. However, accurate standard compounds do not exist to describe the Cu-species present when Cu is interacting directly with the zeolite framework. Recent studies have demonstrated the power of multivariate curve resolution (MCR) methods towards the determination of evolving spectral components in time-resolved XANES datasets^[10,21,28–38]. Multivariate techniques allow for the determination of the pure components within large evolving datasets and as such provide a unique tool for operando spectroscopy. The underlying principle of MCR methods is to decompose a data matrix $D(m \times n)$ of m rows and n columns into matrices of the pure components of the k present species and the time-evolving concentration profiles $C(m \times k)$ and $S^T(k \times n)$ ^[38],

$$D = CS^T + E \quad (3)$$

where the residual of the linear combination result is given by matrix E . By exploiting MCR techniques for the analysis of time-resolved operando XAS studies, the number of significant components, their spectral structure and dynamic evolution can readily be determined. Here, initial determination of the number of significant components has been carried out using the singular value decomposition (SVD) method. However, one should be aware that the SVD method is unable to separate co-evolving components and thus the total number of MCR modelled species may be lower than the actual number of Cu species present in the reaction mixture. The initial spectra have been extracted using the purest variable approach proposed by Windig et al^[39]. Constraints were applied to the MCR analysis such that both the concentrations and spectra are constrained to be non-negative and the total concentration of components sums to unity. Iterative refinement of the initial spectra has been performed until convergence was achieved to yield the pure components. MCR analysis was performed using MCR-ALS developed by Tauler et al^[28] for the simultaneous analysis of multiple experiments following the cut-off and addition of either NH₃ or NO from the reaction mixture at several temperatures (190, 225, 283 and 400 °C). Comparison between the MCR extracted pure components and reference Cu K-edge XANES spectra are shown in Figure 2.

From Figure 2 it is clear that the MCR derived components show a good resemblance to the reference spectra of Cu(NH₃)₂, Cu^{II}(NH₃)₄ and Cu^{II}(NO_x)_y reference Cu complexes previously

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reported^[8] (black, red and blue respectively). The aqueous copper nitrate reference is labelled as $\text{Cu}^{\text{II}}(\text{NO}_x)_y$ due to the negligible difference between the XANES spectra of $\text{Cu}^{\text{II}}(\text{NO}_3)_2$ and $\text{Cu}^{\text{II}}(\text{NO}_2)_x(\text{H}_2\text{O})_{6-x}$ ^[8,40]. $\text{Cu}^{\text{I}}(\text{NH}_3)_2$ and $\text{Cu}^{\text{II}}(\text{NH}_3)_4$ are thought to be related directly to solvated linear Cu^{I} ^[13] and square planar Cu^{II} ^[41] and may not be limited to ligands composing solely of NH_3 ^[19,42]. In the recent work of Negri et al the square planar Cu^{II} species was demonstrated to be composed of mixed ligands^[42]. Herein these species will be described as solvated linear Cu^{I} and square planar Cu^{II} species, respectively.

Figure 2 Comparison of experimental standard XANES spectra and MCR extracted spectra. (a) MCR-ALS derived spectral components. (b) Spectra of reference compounds. The colour assignments of species denote the association of observable spectral components in the reaction scheme shown in Figure 1.

Through a combination of previously reported DFT and XANES studies^[21] the two remaining components can be associated to $\text{Cu}^{\text{I}}\text{-Z}$ and $\text{Cu}^{\text{II}}\text{-Z}$ species directly interacting with the zeolite framework (green and purple, respectively). The two zeolite associated Cu components demonstrate a resemblance to Cu_2O and CuO . In the spectral component assigned to $\text{Cu}^{\text{I}}\text{-Z}$, the presence of Cu^{I} can be noted by the pre-edge peak at approximately 8983 eV associated to the 1s-4p transition^[15,21]. The energy position of the 1s-4p transition has been noted previously to shift dependent on the local coordination of Cu^{I} ^[43–46]. As such a shift between the $\text{Cu}^{\text{I}}\text{-Z}$ and Cu^{I} linearly solvated species attributed species in comparison to the Cu_2O standard is not unexpected and has been previously observed^[47]. Whereas, for the $\text{Cu}^{\text{II}}\text{-Z}$ associated component the absence of this pre-edge peak indicates the presence of Cu^{II} . This demonstrates that MCR analysis of XANES provides a methodology for extracting spectral components that cannot be accurately represented by standard reference compounds.

Previously published work has identified that the Cu in the initial Cu-SSZ-13 catalyst is present primarily as isolated single-site Cu ions that have been recognised as the active species towards $\text{NH}_3\text{-SCR}$ ^[8,16,18,20,23,26] and therefore no metallic Cu component is expected to be present. Whilst the work of Janssens et al^[15] postulates the presence of seven Cu species during the complete reaction scheme, in the work presented here only five distinct species are observed. This may be due to the co-evolution of the two proposed $\text{Cu}^{\text{II}}(\text{NO}_x)_y$ species and two Cu^{I} -solvated species which render them indistinguishable by MCR methods. In addition, the XANES spectra for these species are likely to be indiscernible due to their similar local structures as compared to the identified $\text{Cu}^{\text{II}}(\text{NO}_x)_y$ ^[40] and $\text{Cu}^{\text{I}}(\text{NH}_3)_2$ components. Alternatively, some

Figure 3 Comparison of pure component fraction after switching off NH_3 from the gas feed at time 0. (a-d) Copper speciation resolved from MCR analysis of time-resolved QEXAFS spectra after cut-off of 1000 ppm NH_3 from the gas feed at indicated temperatures. Prior to removing NH_3 from the gas feed, the catalysts were equilibrated under SCR conditions. Concentration fractions for the $\text{Cu}^{\text{II}}(\text{NO}_x)_y$, solvated linear Cu^{I} , $\text{Cu}^{\text{I}}\text{-Z}$, solvated square planar Cu^{II} and $\text{Cu}^{\text{II}}(\text{OH})\text{-Z}$ component species are shown in blue, black, green, red and purple, respectively. (e-h) The concentrations of NH_3 (black) and NO (red) from online mass spectrometry.

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species may be too short lived to accumulate and contribute significantly to the overall XANES spectra. Nonetheless, by only taking into account the here identified five pure components, significant insight into the temperature dependence on the rate-limiting step in the NH_3 -SCR are obtained herein.

After identifying the pure spectral components, MCR has been subsequently used to analyse experiments following the cut-off of NH_3 from and addition of NO to the SCR reaction mixture (1000 ppm NH_3 , 1000 ppm NO, 6 vol% O_2 , 2 vol% H_2O with balance of N_2 , total flow 50 $\text{mL}\cdot\text{min}^{-1}$) at several temperatures. Due to the balance gas flow of N_2 it was not possible to monitor the formation of N_2 using mass spectrometry. The MCR analysis results performed on NH_3 cut-off experiments performed at 190, 225, 283 and 400 °C are given in Figure 3(a-d). At temperatures lower than 283 °C, a significant proportion of solvated linear Cu^{I} species (black) is observed after equilibration under SCR conditions, illustrated as between -60 and 0 s in Figure 3(a and b). This suggests that in the low temperature regime the SCR reaction either proceeds via solvated species^[19,27], or that the SCR reaction is limited at low temperatures by the stability of Cu^{I} -solvated species. Chen et al^[13] previously observed that under similar conditions Cu favours the formation of linear NH_3 -solvated Cu^{I} . At higher temperatures, 283 °C and above, Figure 3(c and d), there is no evidence of solvated species after equilibration under SCR conditions. Instead, an increasing proportion of Cu^{II} -Z (purple) is observed suggesting that Cu is primarily interacting directly with the zeolite framework. The loss of coordinating ligands upon heating has also previously been observed elsewhere^[9,10,48].

Transient speciation changes are observed when the steady-state SCR conditions are perturbed through removal of NH_3 from the gas feed. A transient increase in solvated square planar Cu^{II} species (red) is observed directly subsequent to NH_3 cut-off at 190 and 225 °C. When considering the online mass spectrometry data for 283 °C and below, shown in Figure 3(e-f), it is clear that there is an increase in NO conversion with decreasing proportion of solvated Cu^{I} species between approximately 0 and 200 s after NH_3 cut-off. This suggests that the presence and the low-temperature stability of solvated Cu^{I} species inhibits the conversion of NO. Where the reaction mechanism proceeds via solvated species, the presence of NH_3 in the gas feed may also be limiting the activation of oxygen such as in the mechanisms described by Paolucci et al^[19] and Gao et al^[27]. As such, this observation confirms the conclusion of our former study, that NH_3 locks solvated Cu species to Cu^{I} species thereby hindering its re-oxidation to Cu^{II} and decreasing the SCR activity in the low-temperature regime^[8].

With deconvolution of the Cu^{I} and Cu^{II} zeolite interacting species, as is now possible by MCR analysis, further insight is achieved. Below 400 °C, after the removal of NH_3 from the gas feed, a significant fraction of Cu^{I} -Z is observed to be formed transiently prior to a slow oxidation to Cu^{II} -Z and $\text{Cu}^{\text{II}}(\text{NO}_x)_y$ species. This

behaviour was unobtainable using solely linear combination fitting of standard reference compounds due to the lack of suitable references for the Cu^{I} -Z state. This transient Cu^{I} -Z formation demonstrates that the formation of $\text{Cu}^{\text{II}}(\text{NO}_x)_y$ associated species is very slow at 225 °C and below.

Furthermore, the increase in Cu^{II} -Z species after the peak of the transient Cu^{I} -Z in the low temperature regime provides evidence for the parasitic direct oxidation of Cu^{I} -Z to Cu^{II} -Z. This may be further limiting the conversion of NO by limiting the lifetime of the Cu^{I} -Z state. By following the Cu speciation at 225 °C after NH_3 cut-off in the absence of H_2O in the gas feed this direct oxidation mechanism can be seen more clearly (Figure 4). The experiment performed in the absence of H_2O in the gas feed was not part of the previous publication^[8]. From this experiment it is evident that the formation of Cu^{I} -Z species is transient, rising between 0 and 300 s. Subsequently a further oxidation of Cu^{I} -Z directly to Cu^{II} -Z species occurs 300 s after the cut-off of NH_3 from the gas feed.

Figure 4 XAS derived Cu speciation from MCR analysis of time-resolved QEXAFS after cut-off of NH_3 at 225 °C without H_2O in the gas feed. Concentration fractions for the $\text{Cu}^{\text{II}}(\text{NO}_x)_y$, solvated linear Cu^{I} , Cu^{I} -Z, solvated square planar Cu^{II} and $\text{Cu}^{\text{II}}(\text{OH})$ -Z component species are shown in blue, black, green, red and purple, respectively.

When considering the NH_3 cut-off experiment at 283 °C, the oxidation of initially present Cu^{I} -Z species to Cu^{II} -Z species is not observed to proceed via intermediate states (Figure 3c). This further suggests there is a direct oxidation mechanism at low temperature, which is likely due to the presence of O_2 and H_2O in the gas feed. Alternatively, the lifetime of solvated square planar Cu^{II} species is significantly short enough under SCR conditions such that an observable concentration cannot accumulate in the sample at this temperature and above. The shift towards higher concentrations of Cu^{II} -Z species is further observed at 400 °C (Figure 3d). This suggests a potential change in rate limiting behaviour. At temperatures of 283 °C and above, the reduction of Cu^{II} species rather than the oxidation of Cu^{I} species is favoured

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Figure 5 Comparison of pure component concentrations after adding NO to the SCR gas feed at time 0. (a-d) Copper speciation resolved from MCR analysis of time-resolved QEXAFS after addition of 1000 ppm NO to the gas feed at indicated temperatures. Prior to the addition of NO to the gas feed, the catalysts were equilibrated in 1000 ppm NH₃, 6 vol% O₂, 2 vol% H₂O with balance of N₂. Concentration fractions for the Cu^{II}(NO_x)_y, solvated linear Cu^I, Cu^I-Z, solvated square planar Cu^{II} and Cu^{II}(OH)-Z component species are shown in blue, black, green, red and purple, respectively. (e-h) The concentrations of NH₃ (black) and NO (red) from online mass spectrometry.

in the SCR equilibrated conditions. Due to the reduction of Cu^{II}-Z requiring the presence of NH₃, no significant change in Cu speciation after equilibration is observed at 400 °C when NH₃ is removed from the gas feed.

MCR analysis was also employed on experiments performed to follow the Cu speciation upon initiation of the SCR reaction through the addition of 1000 ppm NO into the gas feed after equilibration under 1000 ppm NH₃, 6 vol% O₂, 2 vol% H₂O with balance of N₂. The results of the multivariate analysis are shown in Figure 5. Under steady state conditions in the absence of NO, a clear trend is apparent: an increase in solvated Cu species with decreasing temperature is observed whilst the proportion of Cu species interacting with the zeolite framework increases with temperature. This further evidences the decreasing ability of NH₃ to form stable solvated linear Cu^I species at elevated temperatures^[49]. Furthermore, at 400 °C prior to the addition of NO to the gas feed, only 300 ppm NH₃ is detected demonstrating that there is a reaction pathway for the direct oxidation of NH₃ in this temperature regime. Under SCR conditions the non-stoichiometric consumption of NH₃ is observed at 400 °C with approximately 70% NO conversion and 100% NH₃ consumption 500 s after the addition of NO to the gas feed. This suggests that the reduction of NO favourably competes with the NH₃ oxidation mechanism but cannot fully explain the NH₃ consumption. The direct oxidation of NH₃ was further investigated using mass spectrometry with a gas composition of 1000 ppm NH₃, 5 vol% O₂ balanced in Ar demonstrating that above 250 °C a partial conversion of NH₃ occurs (Figure S2). Measurement in the absence of the Cu sample confirmed that no gas phase oxidation of ammonia occurs under these operating conditions (Figure S3).

A stoichiometric addition of NO and NH₃ is required for the reduction of Cu^{II}-Z as postulated by the mechanism shown in Figure 1 and equation 1. Therefore, a secondary mechanism, which consumes NH₃, reduces the possibility for Cu^{II}-Z and NO reduction.

Deviating from steady-state conditions, initiation of NH₃-SCR provides significant insight into the rate limiting behaviour at high temperatures. At 400 °C, Cu^{II}-Z species increase steadily concomitant with a decrease in both solvated Cu^I and Cu^I-Z species that were initially present. The rise in the Cu^{II}-Z species at 283 °C is markedly slower than at 400 °C, however from the SCR equilibrated state (Figure 3c) it can be noted that the proportion of Cu^{II}-Z species becomes stable at approximately 40% and equal with the proportion of Cu^I-Z. Considering the equilibrated conditions at 400 °C, it can be noted that Cu^I species dominate the Cu speciation prior to the addition of NO and only upon initiation of the SCR reaction does the proportion of Cu^{II} species rise. This result directly shows that the reduction of Cu^{II}-Z species limits the SCR reaction rate at 283 °C and above. If this were not the case the presence of Cu^I species would remain favoured. This finding complements the NH₃ addition experiments performed at 283 °C and 400 °C, which showed the favourable oxidation of Cu^I to Cu^{II} under SCR equilibrated and NH₃ cut-off conditions. The direct oxidation of NH₃ that is observed prior to NO addition may additionally hinder the reduction of Cu^{II}-Z species under SCR conditions.

Comparison of the initial species present prior to the introduction of NO shows that a clear trend exists between decreasing the proportion of solvated Cu^I and the temperature of the experiment.

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At low temperature (190 and 225 °C, Figure 5a,b), the introduction of NO leads to an increase in concentration of solvated Cu^I species. It has also been noted elsewhere that the strength of reduction is increased in a gas mixture containing both NO and NH₃^[15,48,50]. Furthermore the stability, and as such lifetime, of the solvated Cu^I species is increased by the presence of NO in the gas feed. This may be due to solvated Cu^I species containing both coordinating NH₃ and NO ligands at low temperature, as proposed by the Janssens mechanism (Figure 1)^[15].

However, at higher temperature a marked decrease in solvated Cu^I occurs. At 283 °C (Figure 5c), the proportion of the sample found in the form of zeolite bound Cu^I species increases as the proportion of solvated linear Cu^I decreases^[9,49]. Furthermore, on addition of NO to the gas feed at 283 °C there is a continual rise in the Cu^I-Z proportion. This suggests that the oxidation to Cu^{II}-Z is limiting the SCR reaction in this temperature regime and may explain the dip in SCR activity typically observed between 250 and 350 °C, often denoted as a seagull shape^[8,10,51].

Conclusion

The use of MCR methods for the analysis of time-resolved XAS data allows for an in-depth analysis of the transient Cu speciation in operando experiments probing the NH₃ SCR of NO. Where traditional methods of analysing the XANES spectra rely on linear combination fitting of known standard materials and are limited to cases where suitable standard materials are available, MCR methods are able to establish the number of evolving species and extract pure component spectra for performing linear combination fitting analysis. This allows for the structure of species, otherwise unobtainable from comparison to standard reference materials, to be determined and thus follow their evolution during operando XAS studies.

Experiments following the Cu speciation during NH₃ cut-off have provided clear evidence about the rate limiting steps in the two temperature regimes of the SCR reaction. At temperatures of 283 °C and above the rate of reduction of Cu^{II}-Z to Cu^I-Z species limits the SCR reaction rate. At temperatures lower than 283 °C, the rate limiting step is given by the high stability of solvated Cu^I species.

Coincidental to this finding two parasitic side reactions are observed to take place. In the low temperature regime, there is evidence indicating the direct oxidation of Cu^I-Z to Cu^{II}-Z species occurs, likely due to the presence of O₂ in the gas feed. At high temperatures the over consumption of NH₃ provides evidence that NH₃ can be directly oxidised at temperatures at and above 283 °C. These side reactions may decrease the rate of NO conversion considerably. Between 250 °C and 350 °C, both factors inhibit the SCR reaction and the coupled effect may explain the dip in activity typically denoted by the seagull shape.

Experimental Section

Operando XAS experiments were performed by Marberger et al. and reported partially previously^[9]. The Cu-SSZ-13 catalyst with low metal loading (1.1 wt% Cu, Si/Al = 14, Cu/Al = 0.17) used in this study was prepared as previously described with the low Cu loading chosen to study the dynamic speciation changes^[8]. Around 17 mg of Cu-SSZ-13 (100–150 µm sieve fraction) were firmly fixed between two quartz wool plugs (bed length: 3 mm) in a custom-made cell^[52] used for the operando XAS measurements. Graphite windows (thickness: 0.5 mm) were used on either side of the catalytic bed to ensure X-ray transmission and an air-tight reaction environment. The temperature of the cell was controlled by a thermocouple inserted around 0.5 mm in the catalytic bed from the inlet section of the cell to guarantee homogeneous temperatures over the entire catalytic bed. Mass flow controllers were used to generate a constant flow of the gas mixture (50 mL·min⁻¹; gas hourly space velocity = 100,000 h⁻¹), and automated switch valves (Series 9; Parker, opening response time ≤ 5 ms) that were installed in front of the cell enabled the execution of transient experiments. Stainless steel tubing (1/16 inch) was used throughout; the distance between the switch valves and the middle of the catalyst bed was approximately 100 mm.

Operando XAS measurements were carried out at the SuperXAS beamline of the Swiss Light Source. The storage ring operated at 2.4 GeV in top-up mode with a ring current of 400 mA. The polychromatic X-ray beam resulting from a 2.9 T bending magnet was collimated by a silicon-coated mirror (which also served to reduce higher-order harmonics) and subsequently monochromatised by a Si(111) channel-cut monochromator, which allowed data collection in quick-scanning extended X-ray absorption fine-structure spectroscopy (QEXAFS) mode at 1 Hz. Spectra were collected in transmission mode using 15 cm long N₂-filled ionization chambers. A Cu reference foil mounted between the second and third ionization chamber was measured simultaneously for absolute energy calibration.

The QEXAFS spectra were processed using a bespoke python program to extract individual XAS spectra, calibrate, normalise and interpolate them onto a defined energy grid required for simultaneous multivariate analysis to be performed on all experiments. Multivariate Curve Response analysis was performed using MCR-ALS GUI 2.0.^[34]

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- [1] M. Nachtegaal, O. Müller, C. König, R. Frahm, in *X-Ray Absorpt. X-Ray Emiss. Spectrosc. Theory Appl.*, John Wiley & Sons, Ltd, Chichester, UK, **2015**, pp. 155–183.
- [2] O. Müller, M. Nachtegaal, J. Just, D. Lützenkirchen-Hecht, R. Frahm, in *J. Synchrotron Radiat.*, International Union Of Crystallography, **2016**, pp. 260–266.
- [3] A. J. Dent, *Top. Catal.* **2002**, 18, 27–35.
- [4] M. A. Newton, A. J. Dent, J. Evans, *Chem. Soc. Rev.* **2002**, 31, 83–

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- 95.
- [5] D. Ferri, M. S. Kumar, R. Wirz, A. Eyssler, O. Korsak, P. Hug, A. Weidenkaff, M. A. Newton, *Phys. Chem. Chem. Phys.* **2010**, *12*, 5634–5646.
- [6] S. A. Bates, A. A. Verma, C. Paolucci, A. A. Parekh, T. Anggara, A. Yezerets, W. F. Schneider, J. T. Miller, W. N. Delgass, F. H. Ribeiro, *J. Catal.* **2014**, *312*, 87–97.
- [7] A. M. Beale, F. Gao, I. Lezcano-Gonzalez, C. H. F. Peden, J. Szanyi, *Chem. Soc. Rev.* **2015**, *44*, 7371.
- [8] A. Marberger, A. W. Petrov, P. Steiger, M. Elsener, O. Kröcher, M. Nachttegaal, D. Ferri, *Nat. Catal.* **2018**, *1*, 221–227.
- [9] K. A. Lomachenko, E. Borfecchia, C. Negri, G. Berlier, C. Lamberti, P. Beato, H. Falsig, S. Bordiga, *J. Am. Chem. Soc.* **2016**, *138*, 12025–12028.
- [10] A. R. Fahami, T. Günter, D. E. Doronkin, M. Casapu, D. Zengel, T. H. Vuong, M. Simon, F. Breher, A. V. Kucherov, A. Brückner, et al., *React. Chem. Eng.* **2019**, DOI 10.1039/C8RE00290H.
- [11] J. E. Schmidt, R. Oord, W. Guo, J. D. Poplawsky, B. M. Weckhuysen, *Nat. Commun.* **2017**, *8*, 1666.
- [12] A. Shishkin, H. Kannisto, P.-A. Carlsson, H. Härelind, M. Skoglundh, *Catal. Sci. Technol.* **2014**, *4*, 3917–3926.
- [13] L. Chen, H. Falsig, T. V. W. Janssens, H. Grönbeck, *J. Catal.* **2018**, *358*, 179–186.
- [14] A. G. Greenaway, I. Lezcano-Gonzalez, M. Agote-Aran, E. K. Gibson, Y. Odarchenko, A. M. Beale, *Top. Catal.* **2018**, *1*, 1–8.
- [15] T. V. W. Janssens, H. Falsig, L. F. Lundegaard, P. N. R. Vennestrom, S. B. Rasmussen, P. G. Moses, F. Giordanino, E. Borfecchia, K. A. Lomachenko, C. Lamberti, et al., *ACS Catal.* **2015**, *5*, 2832–2845.
- [16] S. Kawamoto, M. Hirai, M. Kusaka, R. Zhang, J.-S. McEwen, H.-Y. Chen, K. A. Lomachenko, E. Borfecchia, S. Bordiga, A. V. Soldatov, et al., *J. Phys. Conf. Ser.* **2016**, *712*.
- [17] D. Wang, F. Gao, C. H. F. Peden, J. Li, K. Kamasamudram, W. S. Epling, *ChemCatChem* **2014**, *6*, 1579–1583.
- [18] J. Wang, H. Zhao, G. Haller, Y. Li, *Appl. Catal. B Environ.* **2017**, *202*, 346–354.
- [19] C. Paolucci, I. Khurana, A. A. Parekh, S. Li, A. J. Shih, H. Li, J. R. Di Iorio, J. D. Albarracin-Caballero, A. Yezerets, J. T. Miller, et al., *Science (80-)* **2017**, *357*, 898–903.
- [20] C. Paolucci, A. A. Verma, S. A. Bates, V. F. Kispersky, J. T. Miller, R. Gounder, W. N. Delgass, F. H. Ribeiro, W. F. Schneider, *Angew. Chemie - Int. Ed.* **2014**, *53*, 11828–11833.
- [21] A. Martini, E. Borfecchia, K. A. Lomachenko, I. Pankin, C. Negri, G. Berlier, P. Beato, H. Falsig, S. Bordiga, C. Lamberti, *Chem. Sci.* **2017**, *8*, 6836–6851.
- [22] U. Deka, A. Juhin, E. A. Eilertsen, H. Emerich, M. A. Green, S. T. Korhonen, B. M. Weckhuysen, A. M. Beale, *J. Phys. Chem. C* **2012**, *116*, 4809–4818.
- [23] S. T. Korhonen, D. W. Fickel, R. F. Lobo, B. M. Weckhuysen, A. M. Beale, *Chem. Commun.* **2011**, *47*, 800–802.
- [24] D. W. Fickel, R. F. Lobo, *J. Phys. Chem. C* **2010**, *114*, 1633–1640.
- [25] F. Giordanino, E. Borfecchia, K. A. Lomachenko, A. Lazzarini, G. Agostini, E. Gallo, A. V. Soldatov, P. Beato, S. Bordiga, C. Lamberti, *J. Phys. Chem. Lett.* **2014**, *5*, 1552–1559.
- [26] I. Lezcano-Gonzalez, U. Deka, B. Arstad, A. Van Yperen-De Deyne, K. Hemelsoet, M. Waroquier, V. Van Speybroeck, B. M. Weckhuysen, A. M. Beale, *Phys. Chem. Chem. Phys.* **2014**, *16*, 1639–1650.
- [27] F. Gao, D. Mei, Y. Wang, J. Szanyi, C. H. F. Peden, *J. Am. Chem. Soc.* **2017**, *139*, 4935–4942.
- [28] R. Tauler, S. Lacorte, D. Barceló, in *J. Chromatogr. A*, **1996**, pp. 177–183.
- [29] L. Valderrama, R. P. Gonçalves, P. H. Março, D. N. Rutledge, P. Valderrama, *J. Adv. Res.* **2016**, *7*, 795–802.
- [30] A. Voronov, A. Urakawa, W. van Beek, N. E. Tsakoumis, H. Emerich, M. Rønning, *Anal. Chim. Acta* **2014**, *840*, 20–27.
- [31] J. Felten, H. Hall, J. Jaumot, R. Tauler, A. De Juan, A. Gorzsás, *Nat. Protoc.* **2015**, *10*, 217–240.
- [32] M. Fehse, A. Darwiche, M. T. Sougrati, E. M. Kelder, A. V. Chadwick, M. Alfredsson, L. Monconduit, L. Stievano, *Chem. Mater.* **2017**, *29*, 10446–10454.
- [33] L. W. Hantao, H. G. Aleme, M. P. Pedrosa, G. P. Sabin, R. J. Poppi, F. Augusto, *Anal. Chim. Acta* **2012**, *731*, 11–23.
- [34] J. Jaumot, A. de Juan, R. Tauler, *Chemom. Intell. Lab. Syst.* **2015**, *140*, 1–12.
- [35] H. Motegi, Y. Tsuboi, A. Saga, T. Kagami, M. Inoue, H. Toki, O. Minowa, T. Noda, J. Kikuchi, *Sci. Rep.* **2015**, *5*, 15710.
- [36] V. Olmos, L. Benítez, M. Marro, P. Loza-Alvarez, B. Piña, R. Tauler, A. de Juan, *TrAC - Trends Anal. Chem.* **2017**, *94*, 130–140.
- [37] A. Rochet, B. Baubet, V. Moizan, C. Pichon, V. Briois, *Comptes Rendus Chim.* **2016**, *19*, 1337–1351.
- [38] C. Ruckebusch, L. Blanchet, *Anal. Chim. Acta* **2013**, *765*, 28–36.
- [39] W. Windig, D. A. Stephenson, *Anal. Chem.* **1992**, *64*, 2735–2742.
- [40] C. Tyrsted, E. Borfecchia, G. Berlier, K. A. Lomachenko, C. Lamberti, S. Bordiga, P. N. R. Vennestrom, T. V. W. Janssens, H. Falsig, P. Beato, et al., *Catal. Sci. Technol.* **2016**, *6*, 8314–8324.
- [41] J. Chaboy, A. Muñoz-Páez, F. Carrera, P. Merklings, E. S. Marcos, *Phys. Rev. B - Condens. Matter Mater. Phys.* **2005**, *71*, DOI 10.1103/PhysRevB.71.134208.
- [42] C. Negri, E. Borfecchia, M. Cutini, K. A. Lomachenko, T. V. W. Janssens, G. Berlier, S. Bordiga, *ChemCatChem* **2019**, *11*, 3828–3838.
- [43] C. Prestipino, G. Berlier, F. X. Llabrés I Xamena, G. Spoto, S. Bordiga, A. Zecchina, G. Turnes Palomino, T. Yamamoto, C. Lamberti, *Chem. Phys. Lett.* **2002**, *363*, 389–396.
- [44] C. Prestipino, L. Capello, F. D'Acapito, C. Lamberti, *Phys. Chem. Chem. Phys.* **2005**, *7*, 1745–1746.
- [45] C. Lamberti, S. Bordiga, F. Bonino, C. Prestipino, G. Berlier, L. Capello, F. D'Acapito, F. X. Llabrés I Xamena, A. Zecchina, in *Phys. Chem. Chem. Phys.*, **2003**, pp. 4502–4509.
- [46] C. Lamberti, S. Bordiga, A. Zecchina, M. Salvaggio, F. Geobaldo, C. Otero Areán, *J. Chem. Soc. - Faraday Trans.* **1998**, *94*, 1519–1525.
- [47] J. S. McEwen, T. Anggara, W. F. Schneider, V. F. Kispersky, J. T. Miller, W. N. Delgass, F. H. Ribeiro, in *Catal. Today*, **2012**, pp. 129–144.
- [48] B. Kerkeni, D. Berthout, D. Berthomieu, D. E. Doronkin, M. Casapu, J. D. Grunwaldt, C. Chizallet, *J. Phys. Chem. C* **2018**, *122*, 16741–16755.
- [49] E. Borfecchia, C. Negri, K. A. Lomachenko, C. Lamberti, T. V. W.

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- Janssens, G. Berlier, *React. Chem. Eng.* **2019**, *4*, 1067–1080.
- [50] T. Günter, H. W. P. Carvalho, D. E. Doronkin, T. Sheppard, P. Glatzel, A. J. Atkins, J. Rudolph, C. R. Jacob, M. Casapu, J. D. Grunwaldt, *Chem. Commun.* **2015**, *51*, 9227–9230.
- [51] K. Kamasamudram, N. Currier, T. Szailer, A. Yezerets, *SAE Int. J. Fuels Lubr.* **2010**, *3*, 664–672.
- [52] G. L. Chiarello, M. Nachtegaal, V. Marchionni, L. Quaroni, D. Ferri, *Rev. Sci. Instrum.* **2014**, *85*, DOI 10.1063/1.4890668.

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Adam H. Clark*, Rob Jeremiah G. Nuguid, Patrick Steiger, Adrian Marberger, Andrey W. Petrov, Davide Ferri, Maarten Nachtegaal* and Oliver Kröcher

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