Temperature-programmed reduction with NO as a characterization of active Cu in Cu-CHA catalysts for NH3-SCR

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Temperature-programmed reduction with NO (NO-TPR) is introduced as a characterization method, by monitoring the reduction of CuII to CuI in a mixture of NH₃ and NO. Since the NO-TPR method is based on the oxidation and reduction half cycles of the NH₃-SCR reaction, quantitative information about the amount of active Cu in Cu-CHA is obtained. Furthermore, information on the stability and reactivity of reaction intermediates in the NH₃-SCR cycle is obtained as well. The reduction of the Cu is followed by monitoring the consumption of NO, after oxidation of the catalyst in O₂ or a mixture of NO and O₂ to form the CuII state. Two distinct states of the Cu are revealed. The first state, corresponding to the reduction of a Cu oxide species, is reduced around 130 °C and is observed at low Cu content only. The second state corresponds to the reduction of a Cu nitrate species around 200-230 °C. The low-temperature activity of Cu-chabazite catalysts with low Cu content show the same trend as the Cu nitrate species observed in NO-TPR. The fraction of Cu oxide in NO-TPR decreases with increasing Cu content, leading to a non-linear dependence of the NH₃-SCR activity on the Cu content. At high Cu content, all Cu forms a stable Cu nitrate species, and the NH₃-SCR activity becomes proportional to the Cu content. This is agrees well with the known behavior of Cu-CHA catalysts, indicating that NO-TPR seems to be a viable method for the characterization of Cu-CHA materials as NH₃-SCR catalysts.

1 Introduction

The catalytic properties of Cu-CHA materials have been studied extensively during the past decade. The Cu-CHA catalysts typically have a Si/Al ratio in the range 5-20, and the excess negative charge of the zeolite is compensated by positively charged H⁺ and Cu ions. These exchanged Cu ions have the ability to change the oxidation state between CuI and CuII, dependent on the gas atmosphere and temperature.1-8 This implies that these ions have specific redox properties that can be exploited for oxidation catalysis.

The two most studied reactions catalyzed by Cu-CHA are the direct partial oxidation of methane to methanol and the selective catalytic reduction of NO with ammonia in the presence of oxygen (NH₃-SCR).9-17 The direct oxidation of methane to methanol could provide an alternative process for methanol production that circumvents the costly steam-reforming of methane to produce the mixtures of H₂, CO and CO₂, on which the current technology for large-scale methanol synthesis is based.

For NH₃-SCR, Cu-CHA materials are very efficient and robust catalysts, with both a high activity at around 200 °C, and a high hydrothermal stability up to about 700 °C.18,19 These materials are therefore well suited for application in automotive diesel exhaust aftertreatment systems, and are already applied today in heavy-duty vehicles. The Cu-CHA catalyst makes it possible to meet the latest requirements (e.g. Euro 6d) for NOx emissions from diesel engines.

In the NH₃-SCR reaction, the NO and NH₃ react to N₂ and H₂O according to the equation 4 NH₃ + 4 NO + O₂ → 4 N₂ + 6 H₂O. In recent years, significant progress has been made in understanding the mechanism for this reaction.4,7,20-23 The NH₃-SCR reaction cycle can actually be performed stepwise on Cu-zeolite catalysts, by alternating the oxidation and reduction steps, 1,4,20-22 In the reduction step, the Cu starts in the CuII state and is reduced to CuI in a mixture of NO and NH₃, and, dependent on the conditions,
a \([\text{Cu}(\text{NH}_3)_2]^+\)-complex is formed. In the oxidation part, this Cu is reoxidized to a Cu species by a reaction with an NO/O_2 mixture.

The oxidation part of the standard NH_3-SCR reaction involves the dissociation of molecular oxygen, and in the presence of NO, a Cu-nitrate is formed.\(^{5,24,25}\) According to DFT calculations, molecular oxygen is adsorbed exclusively on a Cu species,\(^{4,26,27}\) which implies that a Cu\(^{II}\) species does not contribute to the activation of O_2. The simplest model of oxygen dissociation on a Cu-ion is then that an oxygen molecule adsorbs on a single Cu-ion, where it dissociates. In the presence of NO, this seems a possible reaction path.\(^{26,27}\)

If the O_2 molecule can interact with two Cu\(^{II}\)-ions simultaneously, to form a Cu--O_2--Cu-type of species, the dissociation of the O_2 becomes easier.\(^{21,26,27}\) The activation of oxygen over such a pair of Cu ions seems to be relevant for the NH_3-SCR reaction at low temperatures.\(^{22}\) Under these reaction conditions, the Cu\(^{II}\) species is present as a linear \([\text{Cu}(\text{NH}_3)_2]^+\)-complex,\(^ {5,26,22-27,29}\) and DFT calculations indicate that direct dissociation of the O_2 molecule on a single \([\text{Cu}(\text{NH}_3)_2]^+\)-complex does not occur.\(^{21,22,27}\) The observation that the rate of oxidation of \([\text{Cu}(\text{NH}_3)_2]^+\)-complexes in a CHA zeolite with O_2 shows a second order dependence on Cu-concentration further supports the conclusion that the oxidation of \([\text{Cu}(\text{NH}_3)_2]^+\)-complexes in a CHA-zeolite involves pairs of \([\text{Cu}(\text{NH}_3)_2]^+\)-complexes.\(^{21,22,27}\) The presence of NO also seems to enhance the activation of O_2 on pairs of bare Cu\(^{II}\) ions or \([\text{Cu}(\text{NH}_3)_2]^+\)-complexes.\(^{26,28}\)

An obvious way to form pairs of Cu ions that interact with a single O_2 molecule is by having two Cu ions in positions close enough for a direct interaction with a single O_2 molecule. Since the Cu-ions in the ion-exchange positions in a zeolite are linked to the aluminum atoms, the ability to form Cu pairs increases with decreasing Si/Al ratio in the zeolite. This is part of the explanation why, in general, Cu-zeolites with a Si/Al ratio in the range 5-20 are preferred catalysts for the NH_3-SCR reaction.

After the initial discovery of the possible existence of the \([\text{Cu}(\text{NH}_3)_2]^+\)-complex in Cu-CHA catalysts,\(^5\) it was also realized that this complex is only weakly bound to the zeolite framework, and it therefore becomes mobile.\(^{5,20,21}\) The mobility of the \([\text{Cu}(\text{NH}_3)_2]^+\)-complex is another way to form the Cu pairs that can activate the O_2 molecule. The weak interaction to the zeolite enables the \([\text{Cu}(\text{NH}_3)_2]^+\)-complex to move up to about 9 Å away from its Si-O-Al anchor point in the zeolite framework.\(^ {21,28}\) This means that the actual active sites for O_2 activation in NH_3-SCR are not present in the Cu-CHA material, but are formed dynamically under the influence of the NH_3-SCR conditions, which also allow for the formation of the \([\text{Cu}(\text{NH}_3)_2]^+\)-complex. A consequence is that not all Cu present in the Cu-CHA catalyst necessarily participates in the NH_3-SCR reaction, as the limited mobility will lead to a non-zero probability that a given Cu ion does not find a second Cu atom to form a pair.\(^{21}\) This is a possible explanation for the second-order dependence of the low-temperature NH_3-SCR activity of Cu-CHA catalysts on the Cu content, as observed at low Cu contents.\(^ {20}\) At higher Cu contents, the fraction of unpaired Cu decreases and the activity becomes linearly dependent on the Cu content.\(^ {21}\) A second consequence is that the NH_3-SCR reaction necessarily follows a different mechanism at temperatures where the mobile \([\text{Cu}(\text{NH}_3)_2]^+\)-complex is not stable. This change in reaction mechanism has been proposed as the reason for the decrease in SCR rate with increasing temperature, which occurs around 300 °C and agrees well with the measurement of the thermal stability of the \([\text{Cu}(\text{NH}_3)_2]^+\)-complex.\(^ {7,20,22,27,32}\)

The dynamic formation of the active centers in a Cu-CHA catalyst implies that characterization of the Cu-CHA materials not necessarily gives information that is relevant for the NH_3-SCR reaction. Here, we introduce temperature-programmed reduction with NO (NO-TPR) as a method for exploring the reduction and oxidation properties of Cu-CHA materials that are relevant for NH_3-SCR. The NO-TPR procedure is based on the ability to perform the NH_3-SCR reaction in alternating oxidation and reduction steps, as described above. It has been shown that the reduction in the NH_3-SCR reaction requires the presence of both NH_3 and NO.\(^ {1,4,8}\) By following the consumption of NO under controlled heating in an NO/NH_3 atmosphere, the reduction properties of the Cu for NH_3-SCR in the Cu-CHA catalysts are revealed. The reduction properties of Cu-CHA catalysts have been studied earlier with H_2-TPR, as a method to study the redox properties of Cu-CHA catalysts.\(^ {7,18,33-35}\) Even though the reduction of Cu with H_2 gives some information about the oxidation state of the Cu-CHA materials, the reduction in H_2 is not necessarily relevant in the context of the NH_3-SCR reaction. Since the reduction in a mixture of NO and NH_3 is also part of the NH_3-SCR reaction, the reduction as observed in NO-TPR directly reflects the reduction of the Cu species as it occurs in the NH_3-SCR reaction. Therefore, it is expected that a fraction of Cu not contributing to the NH_3-SCR activity, e.g., due to the limitations to form Cu pairs as discussed above, has a different characteristic in NO-TPR, allowing for a more direct monitoring of the fraction of NH_3-SCR active Cu in Cu-CHA.

In this article, we develop and explore the NO-TPR method in a study of the redox properties of Cu-CHA catalysts for NH_3-SCR. The oxidized and reduced states of the Cu-CHA catalysts are characterized by in situ X-ray Absorption Near-Edge Structure (XANES) spectroscopy and in situ Fourier-transform infrared spectroscopy (FTIR), and the importance of the sample pretreatment in NO-TPR is discussed. Then, to obtain a better insight in the relation between redox properties and NH_3-SCR activity with Cu-content, we present NO-TPR results for a series of Cu-CHA catalysts, based on the same parent material with a Si/Al ratio of 15, with different Cu contents. We show how the reduction properties of Cu-CHA change with Cu content, and relate these to the NH_3-SCR activity at 200 °C (low-temperature activity) of the Cu-CHA catalysts. We show that the ability of Cu-CHA catalysts to form a stable \([\text{Cu}^{II}(\text{NO}_2)]^+\)-species in oxidation in an NO/O_2 mixture follows a similar trend with the Cu-content as the NH_3-SCR activity, suggesting that these \([\text{Cu}^{II}(\text{NO}_2)]^+\)-species indicate the fraction of active Cu in Cu-CHA catalysts.
Table 1 Measured Cu content by ICP and dry matter content, S/I ratio and the corresponding Cu/Al ratio and Cu content on dry matter basis for the catalysts used.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu content</th>
<th>Dry matter</th>
<th>S/I</th>
<th>Cu/Al</th>
<th>Cu content (dry matter basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.717</td>
<td>89.7</td>
<td>15.1</td>
<td>0.123</td>
<td>0.799</td>
</tr>
<tr>
<td>B</td>
<td>1.232</td>
<td>90.7</td>
<td>15.1</td>
<td>0.210</td>
<td>1.358</td>
</tr>
<tr>
<td>C</td>
<td>1.629</td>
<td>89.4</td>
<td>15.1</td>
<td>0.294</td>
<td>1.822</td>
</tr>
<tr>
<td>D</td>
<td>1.93</td>
<td>91.9</td>
<td>15.1</td>
<td>0.328</td>
<td>2.100</td>
</tr>
<tr>
<td>E</td>
<td>2.625</td>
<td>91.5</td>
<td>15.1</td>
<td>0.453</td>
<td>2.869</td>
</tr>
<tr>
<td>F</td>
<td>3.142</td>
<td>90.4</td>
<td>15.1</td>
<td>0.554</td>
<td>3.478</td>
</tr>
</tbody>
</table>

2 Experimental

To characterize the oxidation states of the Cu-CHA catalysts with the NO-TPR procedures, a set of catalysts with S/I ratio of 30, 15, and 5 was used, with a Cu-content of 1.7, 2.1, and 1.8 wt% Cu, respectively. These catalysts were prepared by ion-exchange of the parent materials with a 1.5 mM Cu-acetate solution, followed by calcination at 500 °C for 3 h.

To study the relation between the reduction properties of Cu-CHA catalysts and their NH₃-SCR activity with Cu-content, a second set of six Cu-CHA catalysts with S/I = 15.1 and a Cu content ranging from 0.8 to 3.5 wt% was used. To avoid variations in NH₃-SCR activity not due to Cu-content, this set of catalysts was prepared by Cu-ion exchange of the same H-CHA parent material, thus excluding effects caused by variations in the parent material. Portions of the H-CHA parent material were ion-exchanged with solutions of Cu-acetate with different concentrations in the range 0.5-10 mM, followed by calcination at 500 °C. Table 1 gives a more detailed overview of these catalysts. The Cu content, as measured by ICP, was corrected with the measured dry matter content of the catalyst to obtain the Cu content with respect to the amount of dry zeolite. The dry matter content of the catalysts was determined from measurement of the weight loss upon heating to 200 °C, using a Mettler Toledo HX204 moisture analyzer. The Cu/Al ratio is calculated on the basis of the Cu-content on a dry-matter basis and the known S/I ratio of 15.1 of the parent material, under the assumption that the SI is present as SiO₂, Al is present as Al₂O₃, and Cu is present as CuO. The Cu/Al ratio is then given by:

$$N_{Cu} = \frac{x_{Cu} (N_{Si}M_{SiO_2} + M_{Al_2O_3})}{M_{Cu}x_{Cu}M_{CuO}}$$

(1)

where $N_{Si}$, $N_{Al}$ and $N_{Cu}$ are the molar amounts of Si, Al, and Cu atoms, $x_{Cu}$ is the weight fraction of Cu on a dry-zeolite basis, and M indicates the molar mass for a unit of SiO₂, Al₂O₃, or CuO.

In situ X-ray absorption Near Edge Structure spectroscopy (XANES) experiments were done at the BM23 beamline of the European Synchrotron Radiation Facility (ESRF). The Cu-CHA powder was pressed in a self-supporting wafer with mass optimized for XANES measurements in transmission mode (≈100 mg, resulting in $\Delta \mu x = 0.5$ with total absorption after the edge of $\mu x = 2.5$). The wafer was mounted in a Micronomax reactor cell, equipped with an integrated heating system. The gas atmosphere was controlled by a gas manifold with four gas lines, containing He, O₂, 1% NO/He, and 1% NH₃/He connected to the reactor cell via mass flow controllers, allowing for adjustment of the gas atmosphere. A total flow of 100 Nm³/min was used.

The XANES measurements were done using a double-crystal Si(111) monochromator for the incident energy scan. The incident (10) and transmitted (11) intensities were measured using ionization chambers placed before and after the sample cell. To calibrate the energy scale, a Cu foil reference was measured simultaneously by means of a third ionization chamber (12). The spectra were collected with a constant energy step (6e = 0.5 eV, 0.5 s/step). The presented spectra were normalized to unity edge jump, using the Athena software from the Demeter package.

The in situ FTIR spectra were recorded in transmission mode on a Perkin Elmer System 2000 infrared spectrophotometer, equipped with a MCT detector. For each scan, 128 interferograms, recorded at 2 cm⁻¹ resolution, were averaged. The catalyst powders were pressed in self-supporting pellets of approximately 15 mg and placed inside a commercial FTIR reactor cell (AABBPEC, no. 2000-A multi-mode) with controlled gas atmosphere and temperature. The gas atmosphere in the cell was controlled using a gas manifold similar to that used for the XANES measurements, using He, O₂, 0.1% NO/He, and 0.1% NH₃/He. The flow used in the experiments was 50 Nm³/min.

The measurements of the NH₃-SCR activity and NO-TPR measurements were done in a microreactor setup for powder samples. The reactor is mounted via a 4-way valve that allows for bypassing the reactor. The concentrations of NO, NO₂, N₂O, H₂O, and NH₃ are monitored with an FTIR spectrometer (Gasmet CX4000) at the reactor outlet; the composition of the feed gas is measured by bypassing the reactor.

For the activity measurements, a 5 mg sample (based on dry matter, sieve fraction 150-300 μm) of the catalysts was filled into a quartz U-tube reactor with an inner diameter of 2 mm. Before starting the measurements, the catalysts were heated at 550 °C in 10% O₂/N₂ for 1 h. Then, the feed gas was changed to 225 Nm³/min NH₃-SCR feed gas, consisting of 500 ppm NO, 533 ppm NH₃, 5% water, 10% O₂, and balance nitrogen. The temperature was stepwise lowered to 500, 450, 400, 350, 300, 280, 250, 230, 220, 210, 200, 190, 180, 170, and 160 °C, and at each temperature, the system was allowed to stabilize for 20 min. To evaluate the NH₃-SCR activity, the rate constant for NH₃-SCR at 200 °C is determined from the measured conversion of NO at that temperature, under the assumption that the NH₃-SCR reaction is first order in NO. The rate constant at 200 °C ($k_{200}$) is then given by:

$$k_{200} = \frac{W}{F \ln (1 - X)}$$

(2)

where W is the mass of catalyst, F is the total flow, and X is the conversion of NO. For the NO-TPR measurements, a catalyst powder sample of about 50 or 100 mg on a dry matter basis (150-300 μm sieve fraction) in a quartz U-tube reactor with an inner diameter of 4 mm was used. Various procedures were used for the NO-TPR measurements, which are explained in more detail in the following.
3 The NO-TPR method

The idea behind the NO-TPR experiments is to exploit the possibility of performing the NH$_3$-SCR reaction in separate oxidation and reduction steps. In the first part of the NO-TPR experiment, the Cu is brought in a Cu$^{II}$-state. This typically, but not necessarily, involves exposure of the catalyst to a mixture of NO and O$_2$. The actual NO-TPR measurement is the reduction of this Cu$^{II}$ state in a mixture of NO and NH$_3$ during heating at a predefined rate. The changes in the NO concentration during the reduction give the NO-TPR data. The consumption of NH$_3$ due to reduction of the Cu$^{II}$ is obscured by adsorption and desorption of NH$_3$ on the zelite, and hence, it is difficult to obtain reliable quantitative data on the reduction from the measured NH$_3$ consumption. In contrast, NO interacts weakly with the zelite, and therefore, the reduction of the Cu is clearly observed in the consumption of the NO during reduction.

To ensure a well-defined state of the catalyst in the NO-TPR, the experimental procedure consists of three parts, namely:

1. the preparation of the Cu$^{II}$ state.
2. equilibrating the Cu$^{II}$ state in a mixture of NH$_3$ and NO at 50 °C, the start temperature for the temperature ramp.
3. heating of the catalyst in the NO/NH$_3$ mixture to 370 °C, while recording the consumption of NO.

Variations in the preparation of the Cu$^{II}$ state are possible, and this actually affects the final consumption of NO during the reduction. For the NO-TPR data presented here, the exposure to the NO/O$_2$ mixture is preceded by a reduction step in NO/NH$_3$ at 200 °C, which corresponds to the situation in the NH$_3$-SCR reaction, or by an oxidation in O$_2$ at 500 °C.

We have chosen to start the reduction at 50 °C, which is the lowest practicable temperature in our equipment. Since the NH$_3$-SCR reaction, and therefore also the reduction in the NO/NH$_3$ mixture, is already very effective at 200 °C, the reduction must be started at a significantly lower temperature, in order to detect the NO consumption during reduction. To achieve a well-defined and reproducible state of the catalyst starting the reduction by heating, the Cu$^{II}$-state is equilibrated at 50 °C until the adsorption of NH$_3$ on the zelite is completed, and the measured concentrations of NO and NH$_3$ correspond to the inlet concentrations.

Figure 1 gives an overview of the concentrations of NO, NO$_2$, N$_2$O, NH$_3$ and O$_2$ during the entire procedure for NO-TPR, using 55 mg of catalyst E. The shaded area indicates the steps in the pretreatment of the catalyst, i.e., heating to 500 °C, reduction in NO/NH$_3$ at 200 °C, oxidation in NO/O$_2$ at 50 °C to prepare the Cu$^{II}$ state, exposure to NO/NH$_3$ at 50 °C to equilibrate, and finally the NO-TPR step in NO/NH$_3$ during heating to 370 °C. Immediately before each pretreatment step, the reactor was bypassed to mix the fresh gas to the appropriate concentration, and to measure the composition of the feed gas at each stage. The analysis of the reduction of the Cu-CHA catalyst is based on the consumption of NO during heating to 370 °C (blue curve in red shaded area).

Before turning our attention to the analysis of NO-TPR data, we first discuss a few observations during the different reduction and oxidation before starting the temperature-programmed reduction step. When the NO/NH$_3$-mix is admitted to the reactor at 200 °C in the reduction step, some NO is consumed, indicating that the Cu is in an oxidized state after heating to 500 °C in O$_2$. Simultaneously, a much larger amount of NH$_3$ is consumed, because additional NH$_3$ is consumed for the formation of the linear [Cu(NH$_3$)$_2$]$^{2+}$-complex and adsorption of NH$_3$ on the Brønsted sites in the zelite at 200 °C.

After the reduction at 200 °C, in which the linear [Cu(NH$_3$)$_2$]$^{2+}$-complex is formed, the catalysts are oxidized at 50 °C in a mixture of 2000 ppm NO and 10 % O$_2$, which yields a Cu$^{II}$-(N,O) phase. Figure 1 shows that about 60 ppm NO$_2$ is formed in this mixture, due to the spontaneous oxidation of NO that occurs in the gas phase. Exposing the reduced catalyst to this NO/O$_2$ mixture at 50 °C leads to a further oxidation of NO, to yield approximately 160 ppm of NO$_2$. This increase in NO$_2$ concentration corresponds to the oxidation of NO to NO$_2$ in the confined spaces of the zelite. For this article, it is important to note that some NO$_2$ has been present during this oxidation step, but we do not address this formation of NO$_2$ further.

Finally, before the NO-TPR run can be started, the oxidized Cu$^{II}$-(N,O) phase must be exposed to the mixture of NO and NH$_3$ at 50 °C. The ammonia adsorption that occurs under these conditions leads to the delayed breakthrough of the ammonia. Furthermore, a small amount of NO is consumed initially, together with a larger release of NO$_2$. This shows that at least a part of the Cu$^{II}$-(N,O) phase reacts with NO and possibly also with NH$_3$ at 50 °C, indicating that already at this temperature, some Cu$^{II}$-(N,O) species react with NH$_3$ and NO. The release of NO$_2$, however, is not compatible with a complete NH$_3$-SCR reaction, which only produces N$_2$ and H$_2$O. It may indicate the reaction between a [Cu$^{II}$([NO$_x$])]$^{2+}$ species and NO, which can release NO$_2$ into the gas phase; this reaction would not change the oxidation state of the Cu.$^{24}$

The changes of the Cu-CHA during the NO-TPR procedure
have been verified by the Cu K-edge XANES spectra and FTIR, which are shown in Figure 2. In the Cu-K edge XANES spectrum, the reduction of Cu-CHA at 200 °C in the NO/\text{NH}_3 mixture followed by cooling to 50 °C in He results leads to an intense pre-edge peak at 8983 eV (Figure 2, red). This peak is due to the 1s → 4p transitions in Cu compounds with a low coordination number. This indicates the formation of the [Cu(\text{NH}_3)_2]^{2+}-complex, confirming that the Cu is present as Cu\textsuperscript{2+} at this stage. The formation of the [Cu(\text{NH}_3)_2]^{2+}-complex at is corroborated by FTIR, showing the infrared band at 1620 cm\textsuperscript{-1} related to \text{NH}_3 coordinated to Cu ions. The band at 1446 cm\textsuperscript{-1} and shoulder at 1416 cm\textsuperscript{-1} are due to NH\textsubscript{4}\textsuperscript{+} formed by adsorption of \text{NH}_3 on the Brønsted sites of the zeolite during the reduction at 200 °C.

After subsequent exposure of the [Cu(\text{NH}_3)_2]^{2+}-complex to the NO/O\textsubscript{2} mixture at 50 °C, the characteristic XANES Cu-K pre-edge peak disappears, and a typical spectrum for a Cu\textsuperscript{2+} state is obtained (Figure 2, blue). The appearance of the weak Laporte-forbidden 1s → 3d transition (see inset left panel in Figure 2) is evidence for a Cu\textsuperscript{2+} state. The shape of the XANES spectrum is reminiscent of the spectra obtained upon oxidation in NO/O\textsubscript{2} at 200 °C, which were shown to be due to [Cu(\text{NO})\textsubscript{2}]^{1+}-species. The formation of a nitrate species is clearly observed in FTIR by the bands at 1600 and 1575 cm\textsuperscript{-1}, which is characteristic for a bidentate [Cu(\text{NO})\textsubscript{2}]^{1+}-species. The intense band at 1300 cm\textsuperscript{-1} and the parallel increase at 1445 cm\textsuperscript{-1} indicates the presence of some monodentate nitrate species as well. This means that the exposure of [Cu(\text{NH}_3)_2]^{2+} to a NO/O\textsubscript{2} mixture at 50 °C leads to oxidation of the Cu and formation of a Cu\textsuperscript{II}-(NO\textsubscript{2})-species, probably [Cu(\text{NO})\textsubscript{2}]^{1+}.

Re-exposure of this Cu\textsuperscript{II}-(NO\textsubscript{2})-species to the NO/\text{NH}_3 mixture at 50 °C does not substantially change the oxidation state of the Cu. In the XANES spectrum, the weak 1s → 3d transition is still present, and only a small change is observed in the Cu-K pre-edge region (Figure 2, light blue). The shape of the white line changes and resembles that in the spectra of the [Cu(\text{NH}_3)_2]^{2+}-complex, indicating a change in the first coordination of Cu ions, due to coordination of the Cu by \text{NH}_3. The coordination of the [Cu(\text{NO})\textsubscript{2}]^{1+}-species by ammonia is also observed in FTIR. The band at 1620 cm\textsuperscript{-1}, indicative of coordination of Cu by NH\textsubscript{3}, reappears. The bands around 1300 and 1440 cm\textsuperscript{-1} persist, indicating that monodentate nitrate species still are present. Furthermore, a band at 1385 cm\textsuperscript{-1}, characteristic for ammonium nitrate, appears, while the bands at 1575 and 1600 cm\textsuperscript{-1} for [Cu(\text{NO})\textsubscript{2}]^{1+} disappear. This indicates that the nitrate species becomes more ‘ammonium-nitrate-like’ upon coordination of the Cu with NH\textsubscript{3}. In conclusion, re-exposing the [Cu(\text{NO})\textsubscript{2}]^{1+}-species to the NO/\text{NH}_3 mixture at 50 deg C results in coordination of the Cu by \text{NH}_3, to form Cu\textsuperscript{II}-(\text{NH}_3)_2(\text{NO})\textsubscript{2} complexes (x<4), without a change in the oxidation state of the Cu.

Finally, heating in NO/\text{NH}_3 restores the original [Cu(\text{NH}_3)_2]^{2+}-complex (Figure 2, orange), indicating that the Cu-CHA indeed is reduced the NO-TPR step.

### 4 Results

The results presented above show that the reduction of Cu\textsuperscript{II} in NO/\text{NH}_3 takes place between 50 and 300 °C. Figure 3 shows the NO-TPR profiles of Cu-CHA catalysts with a Si/Al ratio of 30, 15, and 5 and Cu contents of 1, 2, 1, and 1.8 wt%, respectively. For each catalyst, two NO-TPR profiles are shown, obtained by exposing a reduced or oxidized form of the Cu-CHA catalyst to the NO/O\textsubscript{2} mixture at 50 °C. In general, we see that there are two reduction features: a feature around 130 °C, and one around 230 °C; for the catalyst with a low Si/Al ratio, these features appear at ap-
proximately 20 °C higher temperature. The two distinct regions where NO consumption takes place indicate that there are at least two different forms of oxidized Cu that are reduced in the mixture of NO and NH₃; we designate the Cu-species associated with the peak around 130 °C and 230 °C as Cu-a and Cu-b, respectively.

It is clear that the total NO consumption strongly depends on the oxidation state of the Cu catalyst under the exposure to the NO/O₂ mixture to form the Cu(II)-(N₂O)₂-phase. The general trend is that more NO is consumed when the NO/O₂ reacts with a reduced Cu-CHA catalyst. This emphasizes that the pretreatment of the catalyst is important for the final result of the NO-TPR measurement.

In order to measure the amount of Cu participating in the NH₃-SCR reaction, we have adopted a pretreatment procedure that mimics the NH₃-SCR reaction best. In the NH₃-SCR reaction, the O₂ is activated on a Cu-species, and therefore we have chosen a procedure in which the catalysts are first reduced in a mixture of 800 ppm NO and 900 ppm NH₃ at 200 °C, followed by exposure to the NO/O₂ mixture at 50 °C; this is the procedure shown in Figure 1. Figure 4 shows a series of NO-TPR data for the series of Cu-CHA catalysts A-F with different Cu content, as specified in Table 1. The NO-TPR step was done by heating to 370 °C at a rate of 3 °C/min in a mixture of 800 ppm NO and 900 ppm NH₃ with 200 NmL/min.

For the catalysts with a low Cu-content, the two distinct temperature ranges for NO consumption, with peaks at around 130 °C and 230 °C, similar to those shown in Figure 3 for Cu-a and Cu-b. At higher Cu content, the Cu-µ-peak is not observed, and the Cu-b-peak at 230 °C widens towards the low temperature side, with the maximum NO consumption changing to just below 200 °C. The disappearance of Cu-a with increasing Cu content is highlighted in the right panel of Figure 4, clearly showing the change in the shape of the TPR profile with increasing Cu content. The total area under the curves increases with Cu content, which is in line with the expectation that more NO is consumed when more Cu is present.

In the following, we show that Cu-a is a Cu(II)-species that does not contain nitrogen, and that Cu-b is a [Cu(II)(NO₃)]⁺ species, which has already been identified spectroscopically in Figure 2. This assignment is made on the basis of additional NO-TPR measurements, in which the procedure for the formation of the Cu⁺-species has been varied, and a further analysis of the NO-TPR data presented in Figure 4.

Figure 5 presents NO-TPR curves for catalysts B and D, which were measured with and without exposure to the NO/O₂ mixture at 50 °C after oxidation of the Cu at 500 °C in O₂. The NO-TPR curves for catalyst B, with the Cu(II)-(N₂O)₂ species formed from reduced Cu are included as a reference (see also Figure 4). If the exposure to NO/O₂ is omitted in that case, then there is no significant NO consumption. This is expected, since the catalyst has not been oxidized after the initial reduction at 200 °C, leaving the catalyst in the reduced state when performing the NO-TPR measurement.

If the oxidized Cu-CHA catalyst is exposed to the NO/O₂ mixture at 50 °C, the NO-TPR shows both the Cu-µ-peak at 130 °C and the Cu-b peak at 230 °C. At low Cu content (Catalyst B), the Cu-b remains small (catalyst B, 1.35 wt% Cu), but it becomes clearly visible for a catalyst with a higher Cu content (catalyst D, 2.1 wt% Cu). If the exposure to the NO/O₂ mixture at 50 °C is omitted, the peak Cu-b-peak disappears, while the Cu-µ-peak is not affected. These results lead to several important conclusions:

- The Cu-µ species is a nitrogen-containing Cu(II)-species. This is based on the observation that the NO-TPR peak around 230 °C is only observed after oxidation of the catalyst in the NO/O₂ mixture, while it is not present after oxidation in O₂ only.

- The formation of the Cu-µ species is enhanced when the NO/O₂ mixture reacts with the reduced Cu species, probably [Cu(II)(N₂O)₂]⁺, which is formed by reduction in NO/NH₃ at 200 °C. Exposure of Cu(II) to the NO/O₂ mixture at 50 °C results in a significantly smaller NO-TPR peak around 230 °C, indicating a smaller amount of the Cu-µ species.

- The Cu-a species is a Cu(II)-species that does not contain nitrogen, since it is enhanced after oxidation in O₂ at 500 °C, and can also be formed without exposure to the NO/O₂ mixture. This means that the Cu-a species does not react with NO alone. The most obvious candidates for the Cu-a species are Cu(II)-oxide or hydroxide.

We have now established that the Cu-µ species corresponds to a nitrogen-containing Cu(II)-species. A quantitative analysis of the NO-TPR peak at 230 °C indicates that the nitrogen-containing Cu(II)-species is a [Cu(II)(NO₃)]⁺, as follows. By integration of the NO-TPR data shown in Figure 4, the total consumption of NO in the reduction is determined, and compared with the Cu content in the catalysts. From this, the number of NO molecules consumed per Cu atom is determined. Table 2 summarizes these results for the catalysts A-F. We see that the number of consumed NO molecules per Cu atom equals 3 for the catalysts with a higher Cu content (D, E, and F). For the catalysts with a lower Cu-content, the NO/Cu ratio becomes lower. It is noted that precisely the catalysts where the Cu-a species is found also show a NO/Cu ratio lower than 3 here. A graph of these data is given in Figure 4, showing that the catalysts D, E, and F fall on the dashed line, which indicates the stoichiometric NO/Cu ratio of 3.

The stoichiometric NO/Cu ratio of 3 points to the reduction of [Cu(II)(NO₃)]⁺. In an earlier publication, we presented a reaction cycle for NH₃-SCR, in which a [Cu(II)(NO₃)]⁺ species reacts with NO to form a [Cu(II)(NO₃)]⁺ species and an NO₃(g) molecule, followed by further reduction with NH₃ and NO to Cu. According to that reaction cycle, the net reaction for the reduction of the [Cu(II)(NO₃)]⁺ can be written as:

\[
[Cu(II)(NO₃)]⁺ + 3 \text{ NO} + 4 \text{ NH}_3 \rightarrow 4 \text{ N}_2 + 6 \text{ H}_2 \text{O} + [\text{Cu}]^+ \]

Eq. 3 shows that the reduction of a [Cu(II)(NO₃)]⁺ species in an NO/NH₃ mixture requires 3 NO molecules per Cu atom. Therefore, the observed consumption of 3 NO molecules per Cu atom indicates that, for the catalysts with a Cu load above 2 wt% (catalysts D,E,F), all Cu is present as [Cu(II)(NO₃)]⁺ species in
the NO-TPR measurement. The NO-TPR profile for these catalysts show only the presence of the Cu-b species, which therefore can be assigned to the \([\text{Cu}^\text{II}(\text{NO}_3)_2]^{+}\) species. In addition to the spectroscopic identification of the \([\text{Cu}^\text{II}(\text{NO}_3)_2]^{+}\) species given in Figure 2, electron paramagnetic resonance (EPR) measurements also reveal the formation of the \([\text{Cu}^\text{II}(\text{NO}_3)_2]^{+}\) species and the NO/\(\text{Cu}\) ratio in reactions of the \([\text{Cu}^\text{II}(\text{NH}_3)_2]^{+}\)-complex with NO/\(\text{O}_2\) mixtures. Furthermore, the NO consumption in a (\(\text{NH}_3\)+NO)-TPSR measurement on a Cu-CHA catalyst with adsorbed nitrates, which is essentially the same as the NO-TPR measurements presented here, shows a consumption of NO that is quite similar to our curves, especially when the nitrate phase is formed at 120 °C, which is closest to the conditions used here.

We note that Eq. 3 does not contain the \([\text{Cu}^\text{II}(\text{NH}_3)_2]^{+}\)-complex as the \(\text{Cu}\) phase explicitly. The presence of the \([\text{Cu}(\text{NH}_3)_2]^{+}\)-complex, however, can be easily accounted for by balancing the \(\text{NH}_3(g)\) or by the presence of additional \(\text{NH}_3\)-ligands on the \([\text{Cu}^\text{II}(\text{NO}_3)_2]^{+}\)-complex, without affecting the stoichiometric factors for NO and Cu.

The catalysts with a lower Cu content (catalysts A, B, and C) show the presence of the Cu-a species in the NO-TPR profiles (see Figures 4 and 5), which we assign to a Cu\(\text{II}\)-oxide or hydroxide species. This means that for Cu-CHA catalysts with a lower Cu content, not all Cu atoms form a stable \([\text{Cu}^\text{II}(\text{NO}_3)_2]^{+}\) species and the stoichiometric ratio NO/Cu becomes lower than 3. Starting from a \([\text{Cu}^\text{II}(\text{OH})_2]^{+}\)-species, which can be regarded as one half of a dimeric \([\text{Cu}^\text{II}−\text{O}_2−\text{Cu}^\text{II}]^{+}\) species, the reduction to Cu\(\text{II}\) in an NO/\(\text{NH}_3\) mixture can be written as follows:

\[
[\text{Cu}^\text{II}(\text{OH})_2]^{+} + 2\, \text{NO}(g) + 2\, \text{NH}_3(g) \rightarrow 2\, \text{N}_2(g) + 3\, \text{H}_2\text{O}(g) + [\text{Cu}^\text{II}]^{+} \tag{4}
\]

In a similar manner, the reduction of a \([\text{Cu}−\text{OH}]^{+}\)-species, to Cu\(\text{II}\) follows the equation:

\[
2\, [\text{Cu}^\text{II}(\text{OH})]^{+} + 2\, \text{NO}(g) + 2\, \text{NH}_3(g) \rightarrow 2\, \text{N}_2(g) + 3\, \text{H}_2\text{O}(g) + 2\, [\text{Cu}^\text{II}]^{+} \tag{5}
\]

Equations 4 and 5 show that the stoichiometric NO/Cu ratio for the reduction of the Cu-a species is expected to be between 1 and 2, dependent on the type of Cu-oxide species in the catalyst. In any case, this lower than 3, in full agreement with the experimental result (Table 2). Assuming a stoichiometric factor of 1 for the Cu-a species, the total amount of Cu\(\text{II}\), as determined from the NO-TPR data, matches the Cu content obtained with ICP.

---

**Table 2** Total NO consumption (mmol/g) and NO/Cu ratio in NO-TPR of Cu-CHA catalysts, after exposure of reduced Cu-CHA catalysts to a mixture of 800 ppm NO and 900 ppm NH\(_3\), and corresponding conversion of NO and rate constants for NH\(_3\)-SCR.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu cont. (ICP)</th>
<th>Total NO cons.</th>
<th>NO/Cu ratio</th>
<th>NO cons. at 120 °C (Cu-a)</th>
<th>Total Cu(II)</th>
<th>NOx conv. at 200 °C</th>
<th>SCR rate constant (200 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TPR mmol/g</td>
<td>mmol/g</td>
<td>mmol/g</td>
<td>mmol/g</td>
<td>mmol/g</td>
<td>mol/g&lt;\text{scr}&gt; 5 bar</td>
</tr>
<tr>
<td>A</td>
<td>0.126</td>
<td>0.129</td>
<td>1.02</td>
<td>0.07</td>
<td>0.059</td>
<td>0.090</td>
<td>0.039</td>
</tr>
<tr>
<td>B</td>
<td>0.214</td>
<td>0.446</td>
<td>2.08</td>
<td>0.13</td>
<td>0.516</td>
<td>0.225</td>
<td>0.104</td>
</tr>
<tr>
<td>C</td>
<td>0.287</td>
<td>0.602</td>
<td>2.10</td>
<td>0.11</td>
<td>0.492</td>
<td>0.274</td>
<td>0.194</td>
</tr>
<tr>
<td>D</td>
<td>0.339</td>
<td>0.990</td>
<td>3.00</td>
<td>0.03</td>
<td>0.960</td>
<td>0.350</td>
<td>0.230</td>
</tr>
<tr>
<td>E</td>
<td>0.451</td>
<td>1.359</td>
<td>3.01</td>
<td>0</td>
<td>1.550</td>
<td>0.453</td>
<td>0.294</td>
</tr>
<tr>
<td>F</td>
<td>0.547</td>
<td>1.630</td>
<td>2.98</td>
<td>0</td>
<td>1.630</td>
<td>0.543</td>
<td>0.316</td>
</tr>
</tbody>
</table>

* The total amount of Cu\(\text{II}\) is calculated as the sum of the NO consumption at 120 °C and 1/3 of the consumption at 230 °C.
Fig. 5 NO-TPR profiles with and without exposure to the NO/O₂ mixture at 50 °C for oxidized Cu-CHA (catalyst B (black) and D (blue)) and for reduced Cu-CHA (catalyst B (red)). All graphs are drawn to the same scale.

Fig. 6 Total consumption of NO in NO-TPR as a function of the Cu content in Cu-CHA catalysts, after exposure of the reduced state of the Cu-CHA catalysts to a mixture of 800 ppm NO and 900 ppm NH₃. The dashed line corresponds to the stoichiometric ratio NO/Cu of 3.

for all catalysts, except for catalyst A (see Table 2). For catalyst A, the total amount of Cu⁺ determined from the NO-TPR data is lower, indicating that either not all Cu has been oxidized, or that there could be another Cu⁺ phase that is not reduced in the NO/NH₃ mixture at 200 °C.

To relate the NO-TPR results to the low-temperature NH₃-SCR activity of the catalysts A-F, we have measured the NO conversion in the temperature range 160-550 °C, which is shown in the left panel of Figure 7. The left panel in Figure 7 displays the first order rate constants for the NH₃-SCR reaction at 200 °C calculated according to Eq. 2; the values for the NO conversion and rate constants are also included in Table 2. The development of the rate constants with the total Cu content, as determined by ICP, is shown by the red squares in Figure 7, right panel. These data follow the familiar pattern for Cu-CHA catalysts, with a disproportionally low activity for catalysts with low Cu content. This could mean that there exists a critical Cu content for NH₃-SCR activity of Cu-CHA catalysts. There are also indications that the NH₃-SCR activity at low Cu content is proportional to the square of the Cu content, which would also explain this pattern. The latter explanation has led to the conclusion that the NH₃-SCR reaction actually requires pairs of Cu ions, which are formed through diffusion of mobile [Cu(I)(NH₃)₂]⁺-complexes.

The NO-TPR results presented above show that the Cu-CHA catalysts contain both Cu-α and Cu-β species, while catalysts with a high Cu content only have Cu-β. This suggests that the disproportionally low activity of the Cu-CHA catalysts with low Cu content is related to the presence of the Cu-α species, and that only the Cu that is able form a stable [Cu(I)(NO₃)]⁺ contributes to the low-temperature NH₃-SCR activity. To verify this hypothesis, we also compare the rate constants with the amount of Cu-β, which is determined as 1/3 of the amount of NO consumed around 230 °C (see Figure 4 and Table 2). The blue dots in the right panel in Figure 7 show this comparison, and we see, that in the catalysts with low Cu content, the activity becomes proportional to the amount of Cu-β, supporting the hypothesis that only Cu-β contributes to the low-temperature NH₃-SCR activity in these catalysts.

5 Discussion

The NO-TPR results clearly indicate the presence of two types of Cu in Cu-CHA catalysts, that are distinguished by the reaction product of the oxidation of CuI ([Cu(I)(NH₃)₂]⁺) with a mixture of NO and O₂. One type of Cu, Cu-β, forms a stable [Cu(I)(NO₃)]⁺ species, and the other type, Cu-α, forms a Cu-oxide or Cu-OH species. If the Cu content is sufficiently high, all Cu in a Cu-CHA catalyst is Cu-β, while in catalysts with a lower Cu content, some Cu-α is present as well. The low-temperature NH₃-SCR activity is shows the same trend as the [Cu(I)(NO₃)]⁺ (Cu-β) phase in NO-TPR, resulting in a linear correlation with the measured activity in catalysts with low Cu content. Since the formation of [Cu(I)(NO₃)]⁺ is enhanced on a reduced Cu-CHA (Figure 5), it is important that the amount of [Cu(I)(NO₃)]⁺ is measured starting from reduced Cu, to reflect the oxidation step in the NH₃-SCR reaction correctly. The observation that the [Cu(I)(NO₃)]⁺ species is reduced in a NO/NH₃ mixture in the range 150-250 °C implies that it is reactive under typical conditions for NH₃-SCR, and therefore, it cannot be a spectator species in an NH₃-SCR reaction.

The reason for the correlation between Cu-β and the NH₃-SCR activity is that the formation of [Cu(I)(NO₃)]⁺ from CuI or [Cu(I)(NH₃)₂]⁺ is part of the NH₃-SCR reaction cycle. In both the formation of [Cu(I)(NO₃)]⁺ and the NH₃-SCR reaction, the
dissociation of O₂ on the Cu⁰ or [Cu⁰(NH₃)₂]⁺ species is an essential step. Since O₂ does not interact with Cu²⁺ in a Cu-CHA catalyst, activation of O₂ requires a Cu¹ species. The observation that the formation of [Cu²⁺(NO₂)]⁺ is enhanced when the NO/O₂ mixture after reduction of the Cu-CHA catalyst in NO/N₂H₃ (Figure 5) provides direct experimental evidence of this, as the formation of a [Cu²⁺(NO₂)]⁺-species must involve the dissociation of the O₂ molecule. The requirement of a Cu¹ for O₂ dissociation also implies that the rate of NO-oxidation to NO₂ over Cu-CHA does not directly reflect the oxidation properties of Cu-CHA relevant for NH₃-SCR, as the Cu-CHA will contain much less Cu¹ under the conditions for NO-oxidation with O₂, which therefore is much slower.⁴,⁴²

The clear reduction observed in NO-TPR after exposure of a reduced Cu to a mixture of NO and O₂ at 50 °C (Figure 5) indicates that the oxidation of Cu¹ already takes place at that temperature. The reduction associated with the Cu⁺ species, starts between 150 and 200 °C, which is close to the light-off temperature for NH₃-SCR on Cu-CHA catalysts. This would indicate that the oxidation of Cu¹ is easier, which is not consistent with earlier conclusions that the dissociation of oxygen is the rate-limiting step for the NH₃-SCR reaction.⁴,²¹,²²,⁴² It seems that the unavoidable presence of NO₂ in the NO/O₂ mixture is relevant here. NO₂ is more efficient, and therefore, the oxidation of Cu¹ in the NO/O₂ mixture probably is due to oxidation by NO₂. A lower temperature for oxidation of Cu¹ with NO₂, compared to the reduction in NO/N₂H₃, indicates that NO₂ indeed can enhance the rate of the NH₃-SCR reaction to give the fast-SCR reaction. Consequently, the oxidation in NO/O₂ as used in the NO-TPR procedure described in this article corresponds to the oxidation for a fast-SCR reaction, 4 NH₃ + 2 NO + 2 NO₂ → 4 N₂ + 6 H₂O, rather than the standard NH₃-SCR reaction. This would also indicate that the reduction in NO/N₂H₃ becomes rate determined in fast-SCR. Following the reaction mechanism for NH₃-SCR as proposed earlier,⁴ the reduction in standard-NH₃-SCR and fast-SCR follow identical pathways, and therefore, the reduction profiles in NO-TPR as presented here also reflect the reduction as it occurs in the standard NH₃-SCR reaction.

The data in Table 2 show that the total amount of Cu²⁺ determined from NO-TPR, assuming a stoichiometric factor NO/Cu-α of 1, matches the amount found from ICP, indicating that all Cu is oxidized in the NO-TPR measurements. Recently, it has been shown that in oxidation of the Cu¹ species in O₂, some of the Cu¹ phase persists, while oxidation in NO₂ leads to a complete oxidation.⁴¹ Based on this, the conclusion that all Cu has been oxidized in the NO-TPR measurements is also related to the presence of some NO₂ during the oxidation in the NO/O₂ mixture (see Figure 1). This means that at least a part of the Cu²⁺ phase in the NO-TPR experiments is formed by a direct reaction between Cu¹ and NO₂. Then, the oxidic Cu-α species in NO-TPR is the result of a decomposition of a Cu(N,O) species, rather than the product of oxidation by O₂, and consequently, some of the Cu in the Cu-CHA catalyst does not form stable [Cu²⁺(NO₂)]⁺ or other Cu²⁺(N,O) species. For such an oxidic Cu-α species formed by decomposition of Cu²⁺(N,O) species, it can be expected that these do not react further in the NO/O₂ mixture, in line with our conclusion for the Cu-α species in the NO-TPR measurements. An exception is catalyst A, in which there can be a larger contribution of a Cu²⁺O phase, according to Eq. 4, or some reduced Cu may still be present during the NO-TPR measurement, since there is a difference between the amount of Cu²⁺ in NO-TPR and the total amount of Cu found by ICP.

Measurements with electron paramagnetic resonance (EPR) also indicate that, at least at low Cu contents, a part of the visible Cu species remains unaffected upon exposure to NO and O₂, also indicating that not all Cu is able to form a stable [Cu²⁺(NO₂)]⁺.⁴⁰ The fact that such a Cu species is observed in EPR also means that it is a Cu²⁺ species, since Cu¹ species are EPR silent. This matches the assignment of the Cu-α species well: it must be a Cu²⁺ species, because NO-TPR shows that it can be reduced in the NO/N₂H₃ mixture, but it is not affected by the exposure to the NO/O₂ mixture. Furthermore, the Cu-α species is only observed for the Cu-
CHA catalysts with a low Cu content. Therefore, the Cu-α species observed in NO-TPR may very well be the same Cu species that does not form a [Cu(III(NO)₂)]⁺ species in IPR.

An interesting aspect is that increasing the Cu content results in the disappearance of Cu-α, which follows directly from the changes in the NO-TPR profiles around 130 °C, as highlighted in Figure 4. This suggests that a higher fraction of the Cu becomes active with increasing Cu content, and that at only sufficiently high Cu contents (>2 wt%) all Cu contributes to the NH₃-SCR activity. This then results in the known linear dependence of the NH₃-SCR activity with Cu content in this range. Since the fraction of Cu-β increases with the Cu content, the dependence of the NH₃-SCR activity becomes non-linear, with an increasing turnover frequency per Cu atom, as the Cu content increases, in agreement with the known behavior of Cu-CHA catalysts.²¹,²³

6 Conclusions

We have introduced temperature programmed reduction with NO (NO-TPR) as a method to obtain direct and quantitative information about the reduction of the Cu⁰⁸⁸ species in Cu-CHA catalysts. In the NO-TPR procedure, a mixture of NO and NH₃ is used to reduce the Cu⁰⁸⁸ species, and the consumption of NO is measured as a function of the temperature. Since this procedure reflects the reduction part of the NH₃-SCR reaction in Cu-CHA catalysts, the observed reduction profiles are a direct reflection of the relevant reduction properties of Cu for the NH₃-SCR reaction.

The reduction of Cu-CHA catalyst in NO/NH₃ mixtures generally takes place in the temperature range 100-250 °C. Often two peaks are observed, representing the reduction of a Cu-oxide or Cu-hydroxide around 130 °C, and the reduction of a Cu-nitrate ([Cu(NO₃)]⁺) around 200-230 °C. At low Si/Al ratio, the reduction shifts to about 20 °C higher temperature. The results of the NO-TPR measurement further depend on the way the Cu²⁺ phase is prepared, as a consequence of a different reactivity of the NO/O₂ mixture with reduced and oxidized Cu. The general trend is that more Cu-nitrate is formed in a reaction with reduced Cu.

To determine the amount of Cu participating in the NH₃-SCR reaction at low temperatures, good results were obtained by first preparing a Cu⁰⁸⁸ phase in a mixture of 800 ppm NO and 900 ppm NH₃ followed by oxidation at 50 °C in a mixture of 2000 ppm NO in 10% O₂/N₂. The NO-TPR results for series of Cu-CHA catalysts for NH₃-SCR, with different Cu content, ranging from 0.8 to 3.5 wt%, on the same parent material (Si/Al = 15), show a distinction between catalysts with a low and high Cu content.

At high Cu content, the NO consumption in the NO-TPR takes place between 150 and 250 °C, in a broader reduction peak with a maximum consumption at around 200-230 °C. In these cases, the total NO consumption corresponds to exactly 3 times the Cu content in the catalysts, which confirms that all Cu in the catalyst is present as a [Cu(III(NO)₂)]⁺ species, as identified by spectroscopic techniques. This also implies that the [Cu(III(NO)₂)]⁺ species is active under typical SCR conditions.

The low-temperature activity of the Cu-CHA catalysts is related to the amount of stable [Cu(III(NO)₂)]⁺ that is observed in the NO-TPR measurement. For Cu-CHA with a low Cu content, this means that a certain fraction of the Cu does not contribute to the low-temperature NH₃-SCR activity. Increasing the Cu content leads to a gradual increase in the fraction of active Cu, leading to a non-linear dependence of the low-temperature NH₃-SCR activity on the Cu content. At sufficiently high Cu content, all Cu participates in the NH₃-SCR reaction, which is reflected in the amount of stable [Cu(III(NO)₂)]⁺ formed, cleaned by NO₂. This Cu-CHA catalyst displays a linear dependence of the NH₃-SCR activity on the Cu content, in agreement with the known trend of the low-temperature NH₃-SCR activity with Cu content in Cu-CHA catalysts.

Conflicts of interest

There are no conflicts to declare.

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Notes and references
