



# Disproportionation of associated $\text{Cu}^{2+}$ sites in Cu-ZSM-5 to $\text{Cu}^+$ and $\text{Cu}^{3+}$ and FTIR detection of $\text{Cu}^{3+}(\text{NO})_x$ ( $x = 1, 2$ ) species



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## ABSTRACT

Adsorption of NO on an over-exchanged Cu-ZSM-5 sample ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 23$ ) leads to formation of the well-known nitrosyl species of  $\text{Cu}^{2+}$  and  $\text{Cu}^+$ . In addition, two kinds of  $\text{Cu}^{3+}$ -NO mononitrosyls are detected by IR bands at 1960 and 1947  $\text{cm}^{-1}$ . The  $\text{Cu}^{3+}$  species are produced as a result of disproportionation of  $\text{Cu}^{2+}$  ions from associated sites:  $\text{Cu}^{2+}\text{-O-Cu}^{2+} \rightarrow \text{Cu}^+\text{-O-Cu}^{3+}$ . The formation of  $\text{Cu}^+$  ions during NO adsorption is proven with a sample where the preexisting  $\text{Cu}^+$  sites were blocked by CO. In the presence of NO, the  $\text{Cu}^{3+}$ -NO complexes are reduced to  $\text{Cu}^+\text{-NO}$  and  $\text{Cu}^{2+}\text{-NO}$ . At low temperature, the  $\text{Cu}^{3+}$ -NO mononitrosyls are able to accept a second NO ligand forming thus  $\text{Cu}^{3+}(\text{NO})_2$  species (1915 and 1863–53  $\text{cm}^{-1}$ ). The dinitrosyl structures are proven by adsorption of  $\text{NO-}^{15}\text{NO}$  isotopic mixture. The new findings support the hypothesis that  $\text{Cu}^+$  ions are active sites in NO decomposition and the dinitrosyl species, reaction intermediates.

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## 1. Introduction

The problem of  $\text{NO}_x$  emission control is topical for the environmental chemistry. Different technologies for  $\text{NO}_x$  abatement have been applied (e.g., selective catalytic reduction of  $\text{NO}_x$  with ammonia [1,2] and reduction over three-way catalysts [3]) or new routes are now developed (e.g.,  $\text{NO}_x$  storage-reduction [4]). The most attractive way for NO removal seems to be the direct NO decomposition [5–8]. Although still away from practical use, Cu-ZSM-5 is the most studied and promising catalyst for this process [6–24]. Note that this material is also the classic one for the selective catalytic reduction of  $\text{NO}_x$  by hydrocarbons [25]. All this has provoked numerous studies on the nature of the species formed on Cu-ZSM-5 during NO adsorption and its co-adsorption with different reducing agents and/or  $\text{O}_2$  [6–15,17–20,22,26–34]. Despite of the immense efforts, however, the mechanisms of the catalytic  $\text{NO}_x$  reduction processes are still far from well understood.

Many reports on NO adsorption on Cu-ZSM-5 have revealed formation of nitrosyls of  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  cations. The  $\text{Cu}^+\text{-NO}$  species (observed around 1815–1807  $\text{cm}^{-1}$ ) are able to accommodate a second NO molecule being thus converted to dinitrosyls ( $\nu_s$  at ca. 1827 and  $\nu_{as}$  at ca. 1734  $\text{cm}^{-1}$ ) [6–8,10–12,14,15,17–20,22,26,27,29–32,34]. The  $\text{Cu}^{2+}\text{-NO}$  species are typically observed between 1915 and 1895  $\text{cm}^{-1}$ . The exact band position is considered to

depend on the  $\text{Cu}^{2+}$  environment [6,7,10–12,14,15,17–19,22,26,27,31–33]. No dinitrosyls of  $\text{Cu}^{2+}$  have been reported. In addition, formation of surface nitrates and/or nitrites has been noticed by many researches [6–8,10,12,17–23,27,31–34].

There are different mechanisms proposed for NO decomposition on Cu-ZSM-5, many of them involving dinitrosyl species of  $\text{Cu}^+$  [10,19,27]. Indeed, dinitrosyls seem to be appropriate precursor for the formation of N–N bond. However, it is established that  $\text{Cu}^+$  cations are oxidized in the presence of NO [15,18,21,26,27,32]. This fact questions the role of  $\text{Cu}^+$  sites in the NO decomposition process [12].

It was also reported that over-exchanged Cu-ZSM-5 catalysts demonstrated a superior catalytic activity in NO decomposition. This has been related to the existence of associated cations,  $\text{Cu}^{\text{III}}\text{-O-Cu}^{\text{II}}$ , believed to be the most active catalytic centers [12,16,23,24,28].

Concerning the mononitrosyls of  $\text{Cu}^{2+}$  sites, most authors have detected bands at 1915–1905  $\text{cm}^{-1}$ . The common assignment of these bands is to NO adsorbed on isolated  $\text{Cu}^{2+}$  sites in square-pyramidal coordination [14,18,31,32]. Bands at slightly lower frequencies, namely between 1898 and 1894  $\text{cm}^{-1}$ , are usually attributed to  $\text{O}^-\text{-Cu}^{2+}\text{-NO}$  species [7,10,19,30]. It was found that the corresponding  $\text{Cu}^{2+}$  sites are easily reduced and, *vice versa*, formed after oxidation of  $\text{Cu}^+$  sites [14]. Dědeček et al. [14] have distinguished a weak nitrosyl band at 1920  $\text{cm}^{-1}$  but only in the second derivatives of the spectra. The authors assigned this band to NO adsorbed on  $\text{Cu}^{2+}$  ions in square-pyramidal configuration.

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Bands at 1875–1868  $\text{cm}^{-1}$  are assigned to nitrosyls on associated  $\text{Cu}^{2+}$  sites [32,33,35], by analogy with the nitrosyl band detected with copper oxide. Several authors have reported bands at high frequencies, up to 1963  $\text{cm}^{-1}$  [6,8,11,14,18,20,22,34]. In what follows we shall denote the nitrosyl bands in the 1963–1940  $\text{cm}^{-1}$  region as high-frequency (HF) bands. Note that HF bands are reported with other copper-containing materials, as CuY [7,10], Cu-SSZ-13 [36,37], Cu-BEA [37], and Cu-[Al]MCM-41 [38]. There is no consensus on the assignment of the HF bands. Originally, Iwamoto et al. [6,8] have proposed they are due to NO interacting with associated  $\text{Cu}^{2+}$  sites. This assignment was adopted by other researches [22,23,38]. However, HF bands observed with CuY are usually assigned to NO adsorbed on isolated  $\text{Cu}^{2+}$  sites [10]. Some researchers have left the assignment open [20] or have not discussed these bands [18,34]. In most cases, the HF bands have been registered with samples having relatively high copper concentration. Therefore, the original proposal of Iwamoto et al. [6,8] to relate the HF bands to associated copper ions seems reasonable. Note, however, that this is in some disagreement with the assignment of bands around 1880  $\text{cm}^{-1}$  to nitrosyls of  $\text{Cu}^{2+}$  ions from associated sites, as found with CuO [32].

In this work, we report a detailed study of  $^{14}\text{NO}$  adsorption and  $^{14}\text{NO} + ^{15}\text{NO}$  co-adsorption on an over-exchanged Cu-ZSM-5 catalyst paying a special attention to the HF nitrosyl bands.

## 2. Materials and methods

The H-ZSM-5 sample was a commercial Zeolyst product (CBV-2314,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 23$ , BET specific surface area of 425  $\text{m}^2 \text{g}^{-1}$ ). Copper was deposited by ion exchange from aqueous solution at 323 K for 2 h with a 20 mM solution of copper(II) acetate monohydrate (Aldrich, purity 99.8%) using a zeolite/solution ratio of 8  $\text{g l}^{-1}$ . After the ion exchange, the sample was centrifuged, washed twice with double distilled water, and dried at 393 K overnight. It contained 2.96 wt.% copper, which corresponded to an exchange degree of 138%, calculated on the basis of a Cu/Al ratio of 0.5. Further on this sample will be denoted as Cu-ZSM-5.

For comparison purposes, some experiments were performed with two other samples synthesized in analogous way: (i) one sample with a lower exchange degree (54%) and (ii) a sample prepared with another support (Zeolyst 5524G,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$ , BET specific surface area of 425  $\text{m}^2 \text{g}^{-1}$ ) where the copper exchange degree was calculated to be 68%. The results with these two samples are described in Section 3.8.

Before the experiments, the Cu-exchanged samples were treated according to the following procedure: (i) heating under He flow at 5  $\text{K min}^{-1}$  up to 823 K and kept at this temperature for 2 h; (ii) cooling down to room temperature under He flow; and (iii) heating under 1%  $\text{O}_2/\text{He}$  at 5  $\text{K min}^{-1}$  up to 823 K and kept at this temperature for 4 h.

FTIR spectra were registered with a Nicolet Avatar 360 spectrometer. The spectra were recorded accumulating 64 scans at a spectral resolution of 2  $\text{cm}^{-1}$ . Self-supporting wafers from the sample were treated directly in the IR cell. Prior to the adsorption experiments, the sample was activated by 1 h calcination at 673 K followed by 1 h evacuation at 673 K.

NO (purity of >99.0%) was obtained from Messer Griesheim GmbH.  $^{15}\text{NO}$  was purchased from ISOTECH INC. Matheson Tri Gas Company ( $^{15}\text{NO}$  (99%)/He(RG); molar ratio of 1:10). Before adsorption, NO and the isotopic mixture were additionally purified by fractional distillation.

The XRD patterns were registered with a Bruker D8 Advance diffractometer using Cu  $K\alpha$  radiation and a SolX detector.

Copper concentration was quantitatively determined by inductively coupled plasma spectrometry using an Agilent 7500 ICP-MS

instrument. Copper was extracted via MW-assisted dissolution in nitric acid solution.

## 3. Results

### 3.1. Initial characterization of the sample and background spectra

The XRD spectra of the parent zeolite and of the copper-exchanged sample practically coincided and indicated absence of any separate copper oxide phase in Cu-ZSM-5. This conclusion is also supported by the pale-blue color of the copper-containing samples, which was preserved after the IR experiments.

The background spectrum of the parent H-ZSM-5 material ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 23$ ) contains, in the OH region, three bands with maxima at ca. 3744, 3662, and 3610  $\text{cm}^{-1}$  (Fig. S1 from the Supplementary data, spectrum a). The band at 3744  $\text{cm}^{-1}$  is due to external silanols [39,40] and that at 3662  $\text{cm}^{-1}$ , to Al-OH groups [39,40] formed with some EFAL species. The intense band at 3610  $\text{cm}^{-1}$  characterizes zeolite acidic bridging hydroxyls [39,40]. In addition, a broad absorbance centered around 3300  $\text{cm}^{-1}$  is distinguished and indicates the existence of some amount of H-bonded hydroxyls. As already discussed [41], these hydroxyls could be either silanol groups or bridging hydroxyls.

The background spectrum of the Cu-ZSM-5 sample exhibits, in the hydroxyl stretching region, three bands with maxima at 3744, 3668, and 3612  $\text{cm}^{-1}$  (Fig. S1 from the Supplementary data, spectrum b). The band at 3744  $\text{cm}^{-1}$  was already assigned to silanol groups and that at 3668  $\text{cm}^{-1}$ , to Al-OH groups [39,40]. Contribution of some amount of  $\text{Cu}^{2+}$ -OH species to the band at 3668  $\text{cm}^{-1}$  is not excluded [37]. The band at 3612  $\text{cm}^{-1}$  appears with a strongly reduced intensity as compared to the same band detected with the parent zeolite. Based on the integral intensities, it was estimated that about 94% of the bridging hydroxyls have participated in the ion exchange. In addition, the band due to H-bonded hydroxyls vanished from the spectrum of the exchanged material. These results evidence that the principal part of the acidic hydroxyls has participated in the ion exchange.

At 100 K, the hydroxyls bands are slightly shifted and the maxima are set at 3747, 3669, and 3617  $\text{cm}^{-1}$ , respectively (Fig. S1 from the Supplementary data, spectrum c).

### 3.2. Low-temperature CO adsorption

The activated sample was characterized by low-temperature CO adsorption. For comparison, the same experiments were performed with a CO-reduced (5 kPa CO, 15 min, 473 K) sample. It is well known that carbon monoxide forms mono-, di-, and tricarbonyl species with  $\text{Cu}^+$  ions in Cu-ZSM-5 [37,42,43]. The monocarbonyls are characterized by a band at 2157–58  $\text{cm}^{-1}$ , and the dicarbonyls display  $\nu_s$  at 2178  $\text{cm}^{-1}$  and  $\nu_{as}$  at 2151  $\text{cm}^{-1}$ . Bands at 2192 and ca. 2167  $\text{cm}^{-1}$  [42,43] and possibly a band at 2137  $\text{cm}^{-1}$  [42] are typical of tricarbonyl species. With increasing CO coverage, the monocarbonyls are converted into dicarbonyls and then a fraction of the dicarbonyls are transformed into tricarbonyls. Based on  $^{12}\text{C}^{16}\text{O}$ – $^{13}\text{C}^{18}\text{O}$  co-adsorption experiments, it was concluded that a component of the band at 2192  $\text{cm}^{-1}$  (located at 2194  $\text{cm}^{-1}$ ) characterized  $\text{Cu}^{2+}$ -CO species [43].

The carbonyl spectra registered after CO adsorption on activated and reduced sample are compared in Fig. S2 from the Supplementary data. We have chosen three different coverages: (i) at saturation (spectra a and d), (ii) when the tricarbonyls of  $\text{Cu}^+$  are practically destructed (spectra b and e), and (iii) when only monocarbonyls exist on the sample (spectra c and f). The main conclusions based on the experiments are that (i) a significant fraction of  $\text{Cu}^+$  sites exist on the activated sample (ca. 67% of the  $\text{Cu}^+$  sites

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