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Turnover frequency for NO decomposition over Cu-ZSM-5 catalysts: insight into the reaction mechanism ☆

Giuliano Moretti

Centro di Studio del CRN "SACSO", Dipartimento di Chimica,
Università "La Sapienze", Piazzale A. Moro 5, 00185 Rome, Italy

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In this letter we present a simple model useful to understand the relationship between the turnover frequency for NO decomposition over Cu-ZSM-5 catalysts (N_{Cu}), the number of Al atoms per unit cell of the ZSM-5 zeolite (p), and the copper loading expressed as percent of exchange (E). Our simple model is able to explain the literature data. We show that: (1) on catalysts with the highest activity (Cu exchange levels $E > 90\%$), N_{Cu} increases with p (i.e. decreasing the Si/Al ratio) indicating that the most active sites may contain two close copper ions; (2) at low Cu exchange levels ($E < 80\%$) the catalysts have lower activity and, moreover, N_{Cu} decreases with p, according to previous results of Iwamoto et al. (1986). The present results are also in agreement with the evidence that the redox couple Cu^{2+}/Cu^{+} play a key role in the reaction mechanism.

Keywords: NO decomposition; Cu-ZSM-5; turnover frequency; reaction mechanism; MFI-zeolites

1. Introduction

Iwamoto and co-workers [1–3] and Held and co-workers [4] discovered that copper ion-exchanged zeolites, in particular Cu-ZSM-5 zeolites, are active for the catalytic decomposition of NO. It is evident that a deeper insight into the reaction mechanism is important to develop superior catalysts which could find practical applications in the near future [2]. The problems involved in the clarification of the reaction mechanism have been reviewed recently by Hall and Valyon [5] which also have given a comprehensive list of the aspects to be further investigated.

Hall and Vaylon [5] in their reviews of literature results considered of general validity the conclusion reported by Iwamoto et al. in 1986 [1] about the influence of

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the Si/Al ratio on the turnover frequency (N_{Cu}), expressed as twice the number of N_2 molecules produced per copper atom per second.

We recall that Iwamoto et al. [1] reported that the catalytic activity per cupric ion over Cu-ZSM-5 were linearly correlated to the silica–alumina molar ratio of ZSM-5 zeolite (fig. 4 or ref. [1]). This result was based on data obtained at 673 K and with a reaction mixture NO 4% in He. Iwamoto et al. studied catalysts at 40–50% exchange levels to keep conversions low and to treat the system as a differential reactor (by definition 100% of exchange level corresponds to 1 Cu^{2+} per 2 Al atoms). This result was considered correct also for catalysts with exchange levels >90% (the catalysts with the highest turnover frequencies reported up to now) by Shelef [6], by Hall and co-workers [5,7–9], by Spoto et al. [10] and by Giamello et al. [11]. These authors suggested an active site consisting of isolated copper species.

In a previous contribution we have investigated the dependence of NO decomposition activity on Cu loading of Cu-ZSM-5 catalysts [12]. It was found that the very first addition of copper species to ZSM-5 is inactive, then increasing the exchange level up to about 80% leads to catalysts with rather low activity. Conversely the activity of Cu-ZSM-5 catalysts increases by roughly 100-fold when the extent of copper exchange increases from 80 to 100%. We concluded that not all Cu sites are equivalent in their decomposition activity and that 20% is an upper limit for the fraction of Cu which is the most active [11]. It is clear that the Cu active sites with the highest turnover frequency should have a very special configuration. These conclusions are in agreement with experimental results obtained by Hall and co-workers [7,8,13] and Iwamoto and co-workers [1–3]. However, we considered again the effect of the Si/Al ratio on the catalytic activity per site for catalysts with exchange levels >90% [14] and arrived at a conclusion opposite to that reported by Iwamoto et al. [1]. We showed that the most active catalysts, those with copper loadings close to 100% of exchange level or higher, have the lower Si/Al ratios [14]. Several experimental results in agreement with the trend reported in ref. [14] were obtained by Li and Hall [8].

In the present contribution we present a simple model useful to explain the relationship between the turnover frequency (N_{Cu}), the % of copper exchange level (E) and the number of Al atoms per unit cell (p) of the ZSM-5 zeolite. We show that: (1) on catalysts with the highest activity (Cu exchange levels >90%), N_{Cu} increases with p (i.e. decreasing the Si/Al ratio) indicating that the most active sites may contain two close copper ions; (2) at low Cu exchange levels (<80%) the catalysts have lower activity and, moreover, N_{Cu} decreases with p, according to previous results of Iwamoto et al. [1]. The present results are also in agreement with the evidence that the redox couple Cu^{2+}/Cu^{+} play a key role in the reaction mechanism.

2. Results and discussion

In table 1 we report literature data (see also ref. [14]) on the catalytic decomposition of NO over Cu-ZSM-5 catalysts with exchange levels >90%, obtained in the

Table 1
Literature data for nitric oxide decomposition at 773 K over Cu-ZSM-5 catalysts. The rates were obtained under the differential region (conversion to nitrogen normally under 10%) and normalized to NO 4% of an atmosphere. The reaction order in NO is considered to be 1.0 [8]. R_g is the activity per gram of catalyst expressed as twice the number of N_2 molecules produced per gram of catalyst per second; N_{Cu} is the turnover frequency of NO decomposition expressed as twice the number of N_2 molecules produced per Cu atoms per second. The ZSM-5 zeolites are characterized by the Si/Al atomic ratio and by the number of Al atoms per unit cell (p). Copper loading in wt% and as % of exchange (100% corresponds to 1 Cu ion per 2 Al atoms) are also reported. Cu-S represents a catalyst prepared exchanging Cu in silicalite (see ref. [15] for details about the preparation)

Si/Al	p/Al per u.c.	Cu (wt%)	E, % of exchange	$R_g \times 10^{-17}$	$N_{Cu} \times 10^3$	Ref.
11.7	7.56	5.69	152	75.4	14.0	[3]
12.3	7.22	5.04	140	69.7	14.1	[8]
14	6.40	3.12	96	30.9	10.1	[8]
21	4.36	2.54	114	27.1	10.7	[8]
26.4	3.50	2.96	166	19.6	6.65	[8]
77	1.23	1.62	255	8.2	5.34	[15]
Cu-S (silicalite)	0.00	2.03	–	<0.02	<0.01	[15]
Cu/SiO_2	(0.00)	0.86	–	0.0164	0.02	[16]

differential region at 773 K and normalized to NO 4% of an atmosphere. According to Li and Hall [8] a reaction order in NO equal to 1.0 was found. Details about the Cu-ZSM-5 catalysts, i.e. Si/Al atomic ratio, number of Al atoms per unit cell (p), Cu loading expressed both as wt% and as % of exchange level (E) are also reported in table 1. To cover a wider range of p values we have investigated a Cu-ZSM-5 catalyst with $Si/Al = 77, p = 1.23$, and with a copper loading of 1.62 wt% (255% of exchange level), and a Cu-silicalite (Cu-S) sample which had essentially no Al ($p = 0$, Cu 2.03 wt%). Experimental details about the preparation of Cu-ZSM-5 catalysts were reported in refs. [12,13]. More details about the preparation and characterization of the new catalysts used in the present work will be reported in a forthcoming paper [15]. The exchange of copper ions in ZSM-5 ($Si/Al = 77$) and in silicalite was performed in a copper acetate solution 0.1 M at room temperature for 24 h, adjusting the pH of the solution at about 6.5.

All the catalysts reported in table 1 were prepared by ion-exchange in an aqueous Cu(II) acetate. For comparison we also include the result obtained by Hamada et al. [16] on the catalysts Cu/SiO_2 prepared by ion-exchange of silica with an aqueous Cu(II) acetate solution.

Literature data for Cu-ZSM-5 catalysts with exchange levels <90% were reported by Iwamoto et al. [1]. As recalled in the Introduction, Iwamoto et al. studied catalysts at 40–50% exchange levels to keep conversions low and to treat the system as a differential reactor. They found that at these exchange levels the following relationship between the turnover frequency and the number of Al atoms per unit cell:

$$N_{Cu} \approx k_0 - k_1 p \tag{1}$$

with $k_1 << k_0$ (see the data reported in fig. 4 of ref. [1] and consider that $SiO_2/Al_2O_3 = 2Si/Al = 2(96 - p)/p$; N_{Cu} is in arbitrary units (a.u.), $k_0 = 2.6$ a.u. and $k_1 = 0.18$ a.u × no. unit cells / Al atom).

In contrast the results reported in table 1 show that for Cu-ZSM-5 catalysts with exchange levels >90% N_{Cu} increases with p, i.e. decreasing the Si/Al ratio. This result is also shown in fig. 1, where we can see that a plot of N_{Cu} as a function of p is, to a good approximation, linear:

$$N_{Cu} \approx k_2 p\,. \tag{2}$$

We also see that the catalysts Cu/SiO_2 and Cu-S are practically inactive and this confirms the importance of the unique electronic and geometrical structure of the copper sites in Cu-ZSM-5.

As already noted the catalysts reported in table 1 were prepared by ion-exchange in an aqueous Cu(II) acetate solution. It has been shown that both transition metal ion loading and ion-exchange solution pH are critical in determining the specific activity of zeolite catalysts [13,17,18]. This influence has been attributed to the formation of catalytically active metal oxygen bridge species within the zeolite cavities (i.e. M^{n+}–O–M^{n+} species, where the O corresponds to extralattice

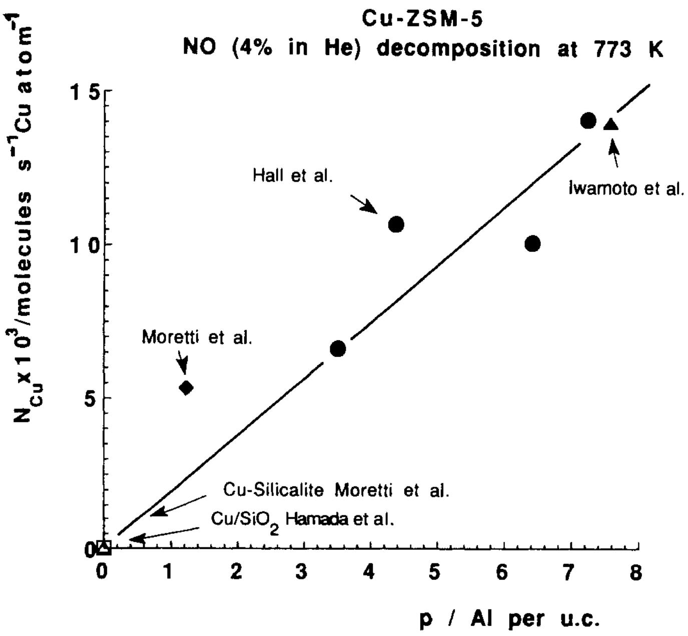

Fig. 1. Turnover frequency (N_{Cu}) for NO decomposition (NO 4% in He) at 773 K of Cu-ZSM-5 catalysts (twice the number of N_2 molecules produced per copper atom per second) as a function of p, the number of Al atom per u.c. of ZSM-5 zeolite. Note that the catalysts have exchange levels >90% (see table 1).

oxide ions). The formation of such species would be expected to be facilitated by high metal loadings and hydrolysis conditions during ion exchange, as is observed experimentally [12,13,17,18]. We also note that these conditions would favour the presence in solution of $Cu(OH)^+$ species which could lead, theoretically, to 200% of exchange level. We note that high values of exchange level (> 100%) could also be explained considering the following possibilities: (1) exchange of polymeric $Cu_x(OH)_y^{(2x-y)+}$ species; (2) precipitation of $Cu(OH)_2$ within the zeolite channels; and (3) exchange of copper species by silanol groups. The points (2) and (3), in particular, are important to explain the exchange of copper ions into silicalite and will be discussed in more detail in a forthcoming paper [15].

The result shown in fig. 1 has a direct relationship with the recent results reported by Iwamoto et al. [19]. These authors used IR spectroscopy combined with an isotopic tracer method, ESR and phosphorescence measurements, to study the adsorption of NO over Cu-ZSM-5 catalysts (with exchange levels close to 100% or higher) to elucidate the mechanism of catalytic decomposition of NO. Iwamoto et al. observed that the intensities of the infrared bands related to the species $(NO)^{\delta-}$ and $(NO)_2^{\delta-}$ decreased at ambient temperature with reaction time, while the intensity of the band related to the species $(NO)^{\delta+}$ increased, according to a *second-order rate equation* [19]. On the basis of these results Iwamoto et al. suggested that dimeric Cu^+ ions could be the active centers, $(NO)^{\delta-}$ and $(NO)_2^{\delta-}$ the intermediates for the decomposition of NO over Cu-ZSM-5 catalysts, and that the catalytic reaction cycle may proceed at high temperature (at least above 573 K), at which oxygen generated through the decomposition can desorb. We note that the result presented in fig. 1 clearly supports dimeric copper sites as the most active in the NO decomposition.

To explain this result as well as the previous result obtained by Iwamoto et al. [1] we consider the following simple model. We write the general equation of the mass balance for copper species (the concentrations of the copper species are referred to a unit cell (u.c.) of ZSM-5 zeolite)

$$[Cu]_t = [Cu_0] + [Cu_1] + 2[Cu_2] + [Cu_{e0}] + [Cu_{e1}] + 2[Cu_{e2}]\,. \qquad (3)$$

In eq. (3) the copper species Cu_0 represent inactive species; the species Cu_1 represent active isolated copper ions; the species Cu_2 represent active dimeric copper ions. The subscript e represents excessively exchanged species (species present at exchange level >100%, by definition). It should be noted that at very high exchange levels in eq. (3) we should include the concentration of the copper species with nuclearity higher than 2, possibly present as polymeric species and as $Cu(OH)_2$. This fact, however, does not change the conclusion of our model because the copper species with high nuclearity dispersed in the zeolite channels are inactive, as demonstrated in ref. [12]. (From the mathematical point of view the concentration of these copper species can be included in $[Cu_0]$).

Note also that the total concentration of copper in the zeolite is related to the % of exchange level (E) and to the number of Al atoms per u.c. (p) by the equation

$$[\mathrm{Cu}]_t = pE/200 \,. \tag{4}$$

According to refs. [1–4,7,8,12,13,15] we can write the following activity order for the turnover frequencies of the several copper species:

$$N_2 \approx N_{e2} >> N_1 \approx N_{e1} >> N_0 \approx N_{e0} = 0 \,, \tag{5}$$

where N_2 and N_{e2} represent the turnover frequencies for NO decomposition of the active sites consisting of two close copper ions: N_1 and N_{e1} represent the turnover frequencies of isolated copper ions; and N_0 and N_{e0} represent the turnover frequencies of inactive copper species (no matter the nuclearity and location of the copper ions in the zeolite).

Now consider first catalysts with exchange levels $<<100\%$. In this case we have

$$[\mathrm{Cu}]_t \approx [\mathrm{Cu}_0] + [\mathrm{Cu}_1] \,, \tag{6}$$

$$N_1 = N_{\mathrm{Cu}}[\mathrm{Cu}]_t/[\mathrm{Cu}_1] \,, \tag{7}$$

where N_{Cu} is the measured turnover frequency. Considering eqs. (4) and (6) and catalysts with about the same E values ($<<100\%$) we can write

$$N_{\mathrm{Cu}} = N_1\{(Ep/200) - [\mathrm{Cu}_0]\}\, 200/Ep \approx N_1 - N_1[\mathrm{Cu}_0]\, 200/Ep \,. \tag{8}$$

Note that eq. (8) can be in agreement with the results obtained by Iwamoto et al. [1] (see eq. (1)) if we assume that: (i) E is a constant; (ii) $[\mathrm{Cu}_0]$ is proportional to p^2; and (iii) $[\mathrm{Cu}_0]$ is always much less than $[\mathrm{Cu}]_t$. In fact assuming that

$$[\mathrm{Cu}_0] = k' p^2 \tag{9}$$

and E = constant, we see that eq. (8) becomes

$$N_{\mathrm{Cu}} = k_0 - k_1 p \tag{10}$$

with $k_1 << k_0$ according to assumption (iii) above.

Actually Iwamoto et al. [1] studied catalysts with high p values ($3.69 < p < 7.50$) and 40–50% of exchange levels for which it can be easily assumed that the small fraction of sites in the ZSM-5 structure that lead to inactive copper species are all filled by copper ions. According to our recent EPR and redox cycles studies [20] as well as from our study of NO decomposition as a function of the copper loading [12], this small fraction of inactive sites is estimated to be of the order of 20% of exchange level for a ZSM-5 zeolite with $p \approx 6$ (even lower % of inactive sites are expected for higher p values). These sites may consist of isolated Cu^{2+} ions that are very difficult to reduce to Cu^{+} probably due to stabilization by a special configuration of the framework oxide ions. These copper species could also be unable to interact with NO and reductants like CO for steric reasons. Considering the ZSM-5 structure we may suggest that the occupation by Al atoms of T12 and T2 sites [21] could be related to the stabilization of the small fraction of inactive Cu^{2+} species. This explains the assumption of eq. (9) because the occupation of two close T2 and

T12 sites, considering a random distribution of Al in the ZSM-5 zeolite, should be proportional to p^2. (Note that the results obtained by Iwamoto et al. and eqs. (9) and (10) lead to $[\mathrm{Cu}_0]$ values in the range of 13–26% of exchange levels (0.24–0.97 copper atoms per u.c.) when p is in the range 7.5–3.7 Al atoms per u.c., in agreement with the results of refs. [12,20].)

The mechanism of NO decomposition on isolated copper species in ZSM-5 has been discussed by several authors [5,6,8–11]. The reduced Cu^+ species play a key role in the formation of mono- and dinitrosyl complexes which evolve towards $\mathrm{Cu}^{2+}\text{---}\mathrm{O}^-$ species by elimination of N_2O. It has been suggested [9] that the transient $\mathrm{Cu}^{2+}\text{---}\mathrm{O}^-$ species leads to the catalytic intermediate $[\mathrm{Cu(NO)(NO_2)}]^+$ (where the copper is in the oxidized Cu^{2+} form) potentially capable to decompose giving nitrogen and oxygen. Note that according to this hypothesis the cyclic reduction of Cu^{2+} to Cu^+ upon evolution of oxygen, by decomposition of the transient $\mathrm{Cu}^{2+}\text{---}\mathrm{O}^-$ species, is not necessary (which is a difficult process to be explained on ZSM-5 where the catalytic sites are far apart from each other).

Now we consider catalysts with exchange levels >100%. In this case according to eq. (5) we can write

$$N_2 \approx N_{\mathrm{e}2} = N_{\mathrm{Cu}}[\mathrm{Cu}]_{\mathrm{t}}/\{[\mathrm{Cu}_2] + [\mathrm{Cu}_{\mathrm{e}2}]\}\,. \tag{11}$$

Assuming that the exchange of $\mathrm{Cu(OH)}^+$ species is responsible for the excessive exchange and considering that a random distribution of Al in the ZSM-5 zeolite implies that

$$[\mathrm{Cu}_2] = k''p^2\,, \quad [\mathrm{Cu}_{\mathrm{e}2}] = k''p^2\,, \tag{12}$$

we can write

$$N_{\mathrm{Cu}} = N_2 2k''p^2\, 200/Ep \approx N_2 2k''p\, 200/E\,. \tag{13}$$

Note that eqs. (11) and (12) can explain the experimental results reported in fig. 1 suggesting that the active sites with the highest turnover frequency may contain two close copper ions. In fact for catalysts with $E \approx 100\%$ ($[\mathrm{Cu}_{\mathrm{e}2}] \approx 0$, ($[\mathrm{Cu}_2] + [\mathrm{Cu}_{\mathrm{e}2}]) \approx k'p^2$) we have

$$N_{\mathrm{Cu}} = N_2 k''p^2\, 200/100p \approx N_2 2k''p = k_2 p\,. \tag{14}$$

A catalyst with $E \approx 200\%$ ($[\mathrm{Cu}_2] + [\mathrm{Cu}_{\mathrm{e}2}]) \approx 2k''p^2$) according to this simple model should have the same activity because

$$N_{\mathrm{Cu}} = N_2 2k''p^2\, 200/200p \approx N_2 2k''p = k_2 p\,. \tag{15}$$

This last result explains the experimental results reported in ref. [12]. Note, however, that some results reported by Valyon and Hall [13] seem to suggest that in certain cases the excessively exchanged ZSM-5 catalysts could be more active with respect to catalysts with exchange levels close to 100%: i.e. it could be that $N_{\mathrm{e}2} > N_2$.

The exchange of dimeric copper species from the solution in ZSM-5 zeolites should be favoured by the presence in the zeolitic framework of sites of the kind Al–O–Si–O–Al. Hunger et al. [22] by means of ^{1}H solid-state NMR studies obtained evidences for such kind of sites at a concentration of 0.2 ± 0.5 per u.c. in H-ZSM-5 zeolites with Si/Al = 15 (6 Al per u.c.). The presence of Al–O–Si–O–Al sites in ZSM-5 is also supported by theoretical calculations [21–24], which indicate that the preferred sites of Al substitution are located in the four-membered (T9) and in the five-membered (T12 and T2) rings. As discussed above the T2 and T12 sites seem to play a role in the stabilization of the inactive Cu^{2+} species at low E values. We suggest that the opposite corners of the four-membered rings (T9 sites) in the sinusoidal channels running parallel to the [100] direction of the ZSM-5 zeolite could be the ideal location of the dimeric copper sites with the highest turnover frequency for NO decomposition. Such T9 sites, after the ion-exchange of copper ions should favour the formation of (Cu^{2+}–O–Cu^{2+}) species. At high temperature it could be possible to invoke the formation of the transient species Cu^+ - - Cu^{2+} - - O^- that in the presence of NO leads to the reaction intermediate (Cu^+(NO) - - Cu(NO_2^-)) which can decompose in N_2 and O_2. This hypothesis avoids the step of oxygen desorption from two Cu^+ - - Cu^{2+} - - O^- sites, which is a difficult process to be explained on ZSM-5 where the catalytic sites are far apart from each other.

The result of fig. 1 shows that superior catalysts could be prepared starting with ZSM-5 zeolites with the lower Si/Al ratios (higher p values) and containing the highest degree of Cu^{2+}–O–Cu^{2+} sites (maximum amount of Al in the T9 sites).

3. Conclusions

A re-examination of literature data shows that the turnover frequency for NO decomposition over Cu-ZSM-5 catalysts with exchange levels >90% increases with the number of Al atoms per u.c. (i.e. decreasing the Si/Al ratio). According to our simple model the results presented in fig. 1 suggest that the most active sites of Cu-ZSM-5 catalysts (lower Si/Al ratio, higher number of Al atoms per u.c., and exchange levels >90%) may consist of *two close copper ions*. Such an active site could serve as a template holding two NO molecules (or at least two nitrogen containing species) which is a necessary requirement for the formation of the N–N bond.

We have also shown that for Cu-ZSM-5 catalysts with exchange levels <90%, where the active sites can be considered isolated copper ions, the turnover frequency decreases with the number of Al per u.c., according to previous results obtained by Iwamoto et al. [1].

The mechanism of the NO decomposition over Cu-ZSM-5 catalysts with exchange levels >90% is therefore very likely that proposed by Iwamoto et al. [19] on the basis of their IR studies of adsorbed NO at room temperature. This is further supported by ^{1}H solid-state NMR [22] and theoretical calculations [21–24] studies of the ZSM-5 zeolites which bring evidences about the existence of Al–O–Si–O–Al sites in the zeolitic framework. Such sites, after the ion-exchange of copper ions should favour the formation of (Cu^{2+}–O–Cu^{2+}) species. The lower activity of the best Cu-Y catalysts should be related to the absence of Cu^+ - - Cu^{2+} - - O^- sites in the supercages, the only place where there is enough room to permit the formation of the reaction intermediate $Cu^+(NO)$ - - $Cu(NO_2^-)$.

Whether the mechanism proposed here will be confirmed by more detailed studies is obviously open to question, but it offers a simple explanation of the result shown in fig. 1. We stress that our ideas represent one interpretation of the data and the result of fig. 1 is, until now, the only experimental support for this picture. The bridged Cu–O–Cu species need to be identified and characterized in more detail (location of the copper species with respect to the zeolitic framework, definition of the local symmetry of the copper species and Cu–O bond lengths). Moreover, a further point to be investigated is related to the transient species $Cu^+(NO)$ - - $Cu(NO_2^-)$ and $[Cu(NO)(NO_2)]^+$ which, according to the proposed mechanisms, at the reaction temperature must release O_2 and N_2 together.

We may add that our recent results in the selective reduction of NO on Cu-ZSM-5 [20] demonstrate that the most active sites seem to be isolated copper species and that these species are also present in Cu-Y. It is evident that the NO decomposition can be considered as a remarkable example of structure-sensitive reaction.

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