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Dimeric Cu(I) species in Cu-ZSM-5 catalysts: the active sites for the NO decomposition

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Abstract

In this study data are presented which support the view that a special configuration of dimeric Cu(I) species in Cu-ZSM-5 catalysts may be the active site for NO decomposition. Such dimeric Cu(I) species, produced by self-reduction of Cu(II) during the thermal activation of Cu-ZSM-5 catalysts in He or under vacuum, are the sites where N_2 is generated from two adsorbed NO molecules, and from which O_2 desorbs from the catalyst at the steady state. It was found that these dimeric Cu(I) species adsorb N_2 irreversibly at low temperature (273–325 K). DFT calculations for cluster models obtained from the crystallographic structure of orthorhombic ZSM-5 suggested that Cu(I)–N_2–Cu(I) species may be IR-silent or have a very low extinction coefficient, as suggested by previous diffuse reflectance FT results. The isosteric heat of adsorption of N_2 on Cu-ZSM-5, obtained with the Clausius–Clapeyron equation from adsorption isotherms in the temperature range of 273–325 K, is 10.3 $\text{kcal}\,\text{mol}^{-1}$ at a coverage of 0.4 mol N_2/mol Cu. This value is much larger than the heat of condensation of N_2 at 77 K (1.33 $\text{kcal}\,\text{mol}^{-1}$) and significantly higher than the heat of adsorption of N_2 on Li-ZSM-5 (8.68 $\text{kcal}\,\text{mol}^{-1}$ at zero coverage) obtained with the Clausius–Clapeyron equation from adsorption isotherms in the temperature range of 196–273 K. The turnover frequency (TOF) for the NO decomposition, calculated assuming that the active sites are those titrated by the irreversible adsorbed N_2 at 273 K, is independent of the copper loading and of the ZSM-5 Si/Al atomic ratio. The present model is also supported by the evidence that Cu-Y, Cu-S-1, and Cu-[Al]-MCM-41 catalysts, containing Cu(I) species that do not adsorb irreversibly N_2 at 273–325 K, were found to be inactive or scarcely active (Cu-Y) for the NO decomposition reaction under the same experimental conditions as employed for Cu-ZSM-5.

Keywords: Cu-ZSM-5; NO decomposition; Dinitrogen adsorbtion; Active site; DFT

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1. Introduction

Nitric oxide is thermodynamically unstable at room temperature (RT) and should decompose according to the reaction $2\text{NO} \leftrightarrows N_2 + O_2$. Such a reaction is thermodynamically favoured up to about 1273 K and could potentially be used for nitric oxide abatement without the addition of any reducing agent. Unfortunately, NO is kinetically very stable. The rate of its thermal homogeneous decomposition below 1273 K is very low, in agreement with the high value of the activation energy for this process (63.8–86 $\text{kcal}\,\text{mol}^{-1}$) [1,2]. It was also noted that even the heterogeneous decomposition is rather slow [1–3]. The strongest proof of this was given by Howard and Daniels, who performed one of the longest experiments in the annals of chemistry [2]. In 1917, they sealed NO in tubes with a random and wide assortment of solid catalysts (main groups and transition metals and their oxides). Inspection of the tubes in 1958 indicated that the decomposition at RT was below 2%, which was also the detection limit of their experiment. The search for good decomposition catalysts continued unsuccessfully until 1986,

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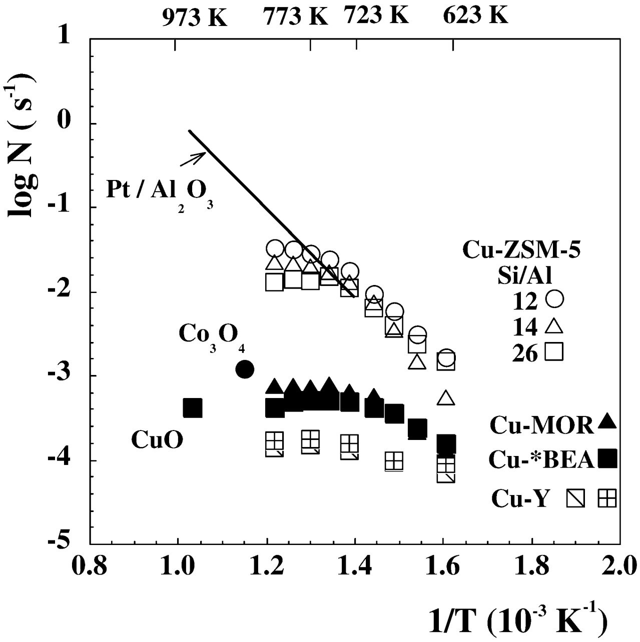

Fig. 1. Arrhenius plot for NO decomposition (NO 4% in He) in the temperature range of 623–973 K. The plot collects data from Refs. [3,6]. The rate is reported for all catalysts but Pt/Al_2O_3 as molecules of NO decomposed to N_2 per second per transition metal atom (TOF, turnover frequency). In the case of Pt/Al_2O_3 the decomposition leads mainly to N_2O and the TOF is reported as molecules of NO decomposed to ($N_2 + N_2O$) per second per Pt atom. To calculate the TOF for CuO, Co_3O_4, Pt/Al_2O_3 it was arbitrarily assumed, according to Ref. [3], that at the surface there are 10^{19} transition metal atoms per square meter. In the case of Cu-zeolites [6], the total amount of copper was considered in the calculation of TOF.

when Iwamoto and co-workers reported that Cu-ZSM-5 was more active by several orders of magnitude than the known catalysts [4].

Whereas many systems (metal oxides, metal supported on oxides, zeolite-based catalysts) are active in the selective catalytic reduction (SCR) of NO_x by hydrocarbons in the presence of oxygen [1,5], Cu-ZSM-5 is unique in its ability to decompose NO into N_2 and O_2 at temperatures between 673 and 773 K. This is indicated by the Arrhenius plot in Fig. 1, where most of the representative literature data [3,6] have been collected. Notwithstanding the high hydrothermal instability, which strongly limits its performance, Cu-ZSM-5 may be considered a “model system” in the research of novel NO decomposition catalysts.

Li and Hall [6] suggested that the spontaneous desorption of O_2 from the catalyst at high temperature is closely related to its steady-state NO decomposition activity, which is the origin of the observed inhibition by O_2 pressure. They also pointed out that the reason for the low efficiency of Cu-ZSM-5 is the maxima in the Arrhenius plot at about 773 K (Fig. 1). Consequently, the conversion cannot be further increased simply by a rise in the temperature. Conversions as high as 100% have been obtained with an increase in the contact time or the catalyst mass, but these are not considered to be reasonable approaches for an industrial application.

As recently reviewed by Pârvulescu et al. [7], an impressive number of publications have been devoted to characterising the Cu-ZSM-5 catalyst with respect to the NO decomposition. However, the nature of the active sites is still unclear and is the subject of extensive debate. On the one hand, it is accepted that the superior activity of the Cu-ZSM-5 catalysts in the NO decomposition can be related to a small fraction of Cu(II) ions that are easily reduced to Cu (I) under vacuum at 723–773 K [6,8] and that these special Cu ions are introduced in the ZSM-5 zeolite only at the higher exchange levels [9,10]. On the other hand, there is no agreement about the number of Cu(I) ions per active site. Shelef [1] and Vaylon and Hall [9] suggested that the reaction occurs on single Cu ions by formation first of the mononitrosyl, then the gem-dinitrosyl, which decomposes into N_2O, leaving an oxygen behind. These authors assumed that the pairing of nitrogens by the interaction of two NO species, each one adsorbed on a different copper site, is unlikely because in high-silica zeolites the copper ions are spaced too far apart. Valyon and Hall noted another important point: two (extraframework) oxygen atoms that are far from each other should still get together to recombine and spontaneously eliminate O_2. How do they migrate on the zeolite surface?

The possibility that the active sites may be pairs of Cu ions rather than the isolated Cu ions, as proposed in the previous schemes, was suggested for two reasons: (i) the TOF of the NO decomposition increases with the copper loading following a peculiar sigmoidal curve with a maximum at about the exchange capacity of the ZSM-5 catalysts [9,10]; (ii) the maximum value of the TOF can be linearly correlated with the number of aluminum atoms per unit cell of the ZSM-5 zeolite [11]. An example of curves TOF versus the copper loading, also showing the effect of the Si/Al atomic ratio of the ZSM-5 matrix and of the inhibition effect of O_2, is shown in Fig. 2 [12]. The present work is aimed at further investigation of the nature of the active sites for the NO decomposition in Cu-ZSM-5. Taking into account previous results [13–15], we report here evidence of the peculiar ability of Cu-ZSM-5 to irreversibly adsorb N_2 at low temperature (273–325 K). As a matter of fact, irreversible N_2 adsorption is not observed when copper is loaded in other matrices (ordered mesoporous silica-alumina, Silicalite-1, zeolite Y) that give inactive (Cu-[Al]-MCM-41 and Cu-S-1) or poorly active (Cu-Y, see Fig. 1 for a comparison with Cu-ZSM-5) catalysts for the NO decomposition. It is well known that N_2 adsorbs *reversibly* on Cu(I) species at RT with on-top symmetry, giving a N≡N stretching vibration at 2295 cm^{-1} that disappears on evacuation [16,17a,b]. We found that Cu-ZSM-5 catalysts also adsorb N_2 in an *irreversible* way at 273–320 K [13–15]. Similar results were reported by Kuroda and co-workers [17c–g]. The irreversibly absorbed N_2 was found to be IR silent, suggesting a symmetric coordination to dimeric Cu(I) species [15]. To improve the knowledge of the irreversible N_2 species, we report here (i) new adsorption and catalytic data, (ii) the isosteric heat of adsorption of irreversible N_2, and (iii) DFT calculations on the electronic

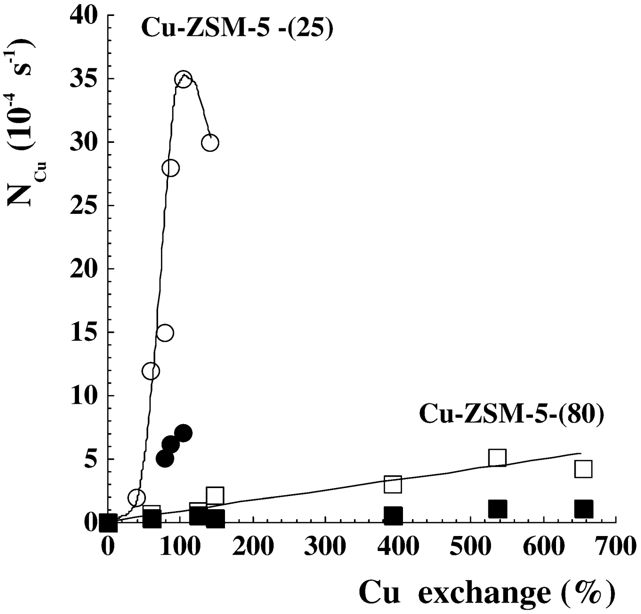

Fig. 2. TOF for NO decomposition (NO 0.5% in He; open symbols) at 773 K on Cu-ZSM-5 with Si/Al = 25 and 80 as a function Cu exchange %. Together with the effect of the Si/Al atomic ratio of the ZSM-5 zeolite, it is also shown the inhibition effect of O_2 (NO 0.5%–O_2 1% in He; solid symbols). The data are taken from Ref. [12].

and geometrical properties of Cu(I)–N_2–Cu(I) complexes on cluster models obtained from the crystallographic structure of orthorhombic ZSM-5 [18]. The correlation found between the irreversible adsorption of N_2 at low temperature (273–320 K) and the catalytic data for the NO decomposition in Cu-ZSM-5 suggest a new structure for the active site.

2. Experimental

The zeolite (NaY, H-ZSM-5, S-1) and ordered mesoporous silica-alumina ([Al]-MCM-41) starting materials were the same as some of those used in previous studies [10, 12–15,19,20]. Copper was introduced into H-ZSM-5 with Si/Al = 25 and Si/Al = 80 (and into NaY, [Al]-MCM-41, Si/Al = 30, S-1) by the ion exchange method with copper nitrate solutions (0.01 or 0.1 M, pH ca. 4) and copper acetate solutions (0.01 or 0.1 M, pH ca. 5.5). In each preparation 2 g of zeolite was brought into contact, generally at RT, with 250 ml of copper salt solution for 2 h under stirring. To obtain overexchanged catalysts (Cu/Al > 0.5) the exchange was repeated two or three times with 0.1 M solutions. More details about the preparation and physicochemical characterisation of the catalysts have been reported previously [10, 12–15,19,20]. The fresh catalysts were treated at 823 K in air for 4 h before the adsorption measurements and the tests of catalytic activity. The samples were identified according to an accepted conventional code: Cu-ZSM-5-(Si/Al ratio)-Cu exchange % (and/or Cu wt%). The measurements of nitrogen adsorption in the temperature range of 273–325 K were performed with a Micromeritics ASAP 2010 automatic analyser. After the above treatment in air, the samples were outgassed for 24 h at 823 K at a reduced pressure of ca. 7.5×10^{-6} Torr (1 Torr = 133.3 Pa).

The amount of nitrogen irreversibly adsorbed at 273–325 K was evaluated with the double isotherm method in the P_{N_2} range of 0–120 Torr. The isosteric heat of adsorption was determined by application of the Clausius–Clapeyron equation to the adsorption isotherms measured at 273, 293, and 313 K. The Cu(II) species in Cu-ZSM-5-(25) catalysts that undergo self-reduction by thermal treatment in vacuum at 823 K were titrated by measurements of irreversible CO adsorption at RT in a BET-type apparatus, according to a well-established method [21].

The catalytic tests were carried out in flow mode with the effluent gas analysed with an on-line gas chromatograph equipped with an Alltech CTR-1 column and a hot wire detector. The catalysts (ca. 100 mg) underwent the standard pretreatment in flowing 10% O_2 in He at 773 K overnight. The reactant blend (0.46% NO in He) was passed at atmospheric pressure through the catalysts at a flow of 100 ml (NTP)/min (GHSV = 30,000 h^{-1}) at a temperature range of 423–823 K with a 0.5-h isothermal step at any selected temperature.

Theoretical DFT calculations were made to investigate the N_2 and O_2 adsorption on single and dimeric Cu(I) ions within the ZSM-5 framework. All calculations were performed by the Gaussian 98 code [22] with the use of the B3LYP [23,24] functional. The Ahlrichs' basis sets SVP [25] was used for geometry optimisation, and the more extended TZVP [26] was used for energy calculations. In the latter case, polarisation functions were added only to non-hydrogen atoms, namely, N, O, Al, Si, and Cu, whereas H was given the TZV basis set. The cluster models used in the calculations were extracted from the crystallographic structure of orthorhombic H-ZSM-5 [18]. The composition of each cluster, with the corresponding numbering of Si and Al atoms with respect to the asymmetric unit of ZSM-5 [18], is indicated in Tables 1 and 2. According to the Loewenstein rule, the Al–O–Al configuration was not considered. Geometry optimisation was performed only on the coordinates of Cu, adsorbed N_2 and O_2, leaving Al, Si, and framework O frozen in their crystallographic positions. Dangling bonds of the terminal O atoms were passivated by H atoms placed 1.0 Å in the direction of the next framework Si atom. All optimised geometries were vibrationally characterised. The interaction energy of N_2 and O_2 on Cu(I) centers in the ZSM-5 structure was corrected for the BSSE according to the Boys–Bernardi counterpoise method [27], in the formulation reported by Tuma et al. [28].

3. Results

Some representative N_2 adsorption isotherms measured at 273 K on Cu-ZSM-5 with Si/Al = 25 and 80 are reported in Figs. 3 and 4, respectively. The isosteric heat of adsorption

Table 1
DFT results for N_2 adsorption on different clusters extracted from the ZSM-5 crystallographic structure. Geometry of N_2 coordination to Cu(I), cluster employed for the calculation, Si/Al position within the ZSM-5 structure [18] (Al position in bold), BSSE-corrected B3LYP/TZVP[a]//B3LYP/SVP interaction energy (E_{int}) of the N_2 molecule, calculated shift of the N≡N stretching with respect to gas-phase N_2 (2490 cm^{-1} is the B3LYP/SVP calculated Raman value), IR intensity (extinction coefficient) of the N≡N stretching and optimized distance between Cu(I) ions.

N_2 coordination	Cluster	Si/Al position	E_{int} (kcal mol^{-1})	IR shift (cm^{-1})	IR intensity (km mol^{-1})	r(Cu–Cu) (Å)
Single Cu(I)						
η^1-N_2	$Al(OH)_4Cu–N_2$[b]		−18.5	−90	230	
Cu(I) pairs						
[010] channel						
μ-η^1:η^1-N_2	$Al_2(OH)_8Cu_2–N_2$	**2**, **8**	−36.5	−194	27	4.79
μ-η^1-N_2	$Al_2Si_2(OH)_{10}Cu_2–N_2$	**11**, 10, 10, **11**	−9.3	−227	325	2.38
μ-η^2:η^2-N_2	$Al_2Si_2(OH)_{10}Cu_2–N_2$	**11**, 10, 10, **11**	−2.0	−501	415	2.53
[100] channel						
cis-μ-1,2-N_2	$Al_2Si_2(OH)_{10}Cu_2–N_2$	**6**, 9, 9, **6**	−35.1	−196	184	4.31
cis-μ-1,2-N_2	$Al_2(OH)_8Cu_2–N_2$	**6**, **6**	−29.1	−211	228	4.11
μ-η^1-N_2	$Al_2Si(OH)_8Cu_2–N_2$	**9**, 9, **6**	−20.2	−220	302	2.49

[a] Polarization functions only on non-hydrogen atoms.
[b] Full geometry optimization without ZSM-5 lattice constraints.

Table 2
DFT results for O_2 adsorption on different clusters extracted from the ZSM-5 crystallographic structure. Geometry of O_2 coordination to Cu(I), cluster employed for the calculation, Si/Al position within the ZSM-5 structure [18] (Al position in bold), BSSE-corrected B3LYP/TZVP[a]//B3LYP/SVP interaction energy (E_{int}) of the O_2 molecule, calculated shift of the O=O stretching with respect to gas-phase O_2 (1697 cm^{-1} is the B3LYP/SVP calculated Raman value), IR intensity (extinction coefficient) of the O=O stretching and optimized distance between Cu(I) ions.

O_2 coordination	Cluster	Si/Al position	E_{int} (kcal mol^{-1})	IR shift (cm^{-1})	IR intensity (km mol^{-1})	r(Cu–Cu) (Å)
Single Cu(I)						
η^2-O_2	$Al(OH)_4Cu–O_2$[b]		−19.8	−411	196	
η^1-O_2 (bent)	$Al(OH)_4Cu–O_2$[b]		−13.7	−244	458	
Cu(I) pairs						
[010] channel						
trans-μ-1,2-O_2	$Al_2(OH)_8Cu_2–O_2$	**2**, **8**	−83.2	−573	92	4.83
μ-η^2:η^2-O_2	$Al_2Si_2(OH)_{10}Cu_2–O_2$	**11**, 10, 10, **11**	−29.2	−760	89	2.58
[100] channel						
trans-μ-1,2-O_2	$Al_2Si_2(OH)_{10}Cu_2–O_2$	**6**, 9, 9, **6**	−37.7	−586	318	4.07
trans-μ-1,2-O_2	$Al_2(OH)_8Cu_2–O_2$	**6**, **6**	−38.9	−607	238	4.06
μ-η^1-O_2	$Al_2Si(OH)_8Cu_2–O_2$	**9**, 9, **6**	−34.3	−491	349	2.50

[a] Polarization functions only on non-hydrogen atoms.
[b] Full geometry optimization without ZSM-5 lattice constraints.

was determined from the adsorption isotherms on Cu-ZSM-5-(25)-104 (Cu 1.97 wt%) measured at 273, 293, and 313 K. A value of 10.3 kcal mol^{-1} (1 kcal = 4.184 kJ) was calculated for a coverage of 0.4 mol of total N_2/mol of Cu. The heat of adsorption of N_2 obtained by calorimetry on Cu-ZSM-5 catalysts as a function of N_2 coverage was reported by Kuroda and co-workers al. for the first and second adsorption isotherms measured at RT [17f–g]. The value extrapolated at zero N_2 coverage is ca. 19 kcal mol^{-1}, in good agreement with our calculated values for several site geometries reported in Table 1 (vide infra). Moreover, a good agreement is found between our experimental value and the heat of adsorption derived at similar coverage (0.4 mol N_2/mol Cu) from the heat of adsorption versus N_2 adsorbed volume plot reported by Kuroda and co-workers [17g].

Yamazaki et al. [29] reported the heat of adsorption of N_2 in the temperature range of 196–273 K (extrapolated at zero coverage) over S-1 (3.87 kcal mol^{-1}), H-ZSM-5 (3.97 kcal mol^{-1}), and M-ZSM-5 with M = Li, Na, K, Rb, and Cs (8.68, 6.67, 5.66, 5.16, and 4.97 kcal mol^{-1}, respectively).

The self-reduction of Cu(II) species in Cu-ZSM-5 after treatment at high temperature in vacuum, or under inert flowing gas, is a well-known phenomenon [6,8]. The effect of the self-reduction on the Cu-ZSM-5-(25) catalysts treated at 823 K in vacuum as a function of the copper loading is shown in Fig. 5. The upper curve shows the Cu(I)/Cu_{tot} ratio, that is, the fraction of the total copper reduced and titrated by the irreversible adsorption of CO at RT ($(CO)_{irr}$ = Cu(I)), a well-established technique for counting the exposed Cu(I) species [21]. It is evident from the data in Fig. 5 that, independently of the copper loading, about 80% of the copper species in Cu-ZSM-5-(25) catalysts is involved in the self-reduction process. Kuroda et al. reported similar

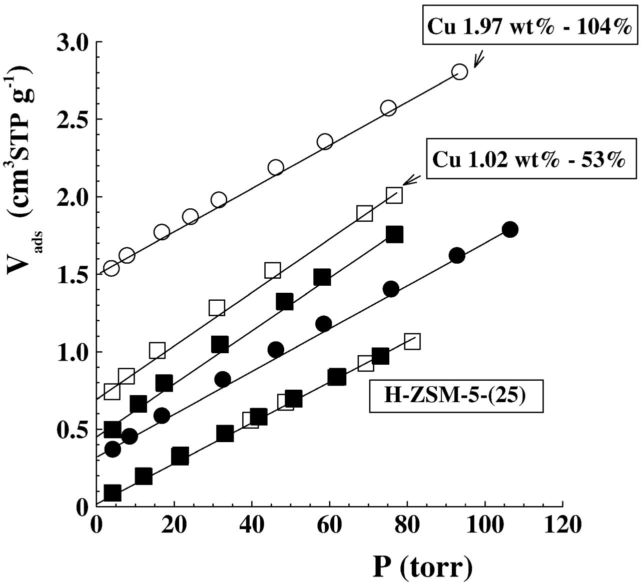

Fig. 3. N_2 adsorption isotherms at 273 K on Cu-ZSM-5 (Si/Al = 25). Two Cu-ZSM-5 samples are reported with copper exchange 53 and 104%. The pure H-ZSM-5 (Si/Al = 25) zeolite is reported for comparison. The open symbols are relative to the first adsorption isotherm. The second adsorption isotherm (solid symbols) was measured after evacuation at 7.5×10^{-6} Torr for 30 min at 273 K. The irreversibly adsorbed N_2 is the difference between the first and the second adsorption isotherm at $p = 0$.

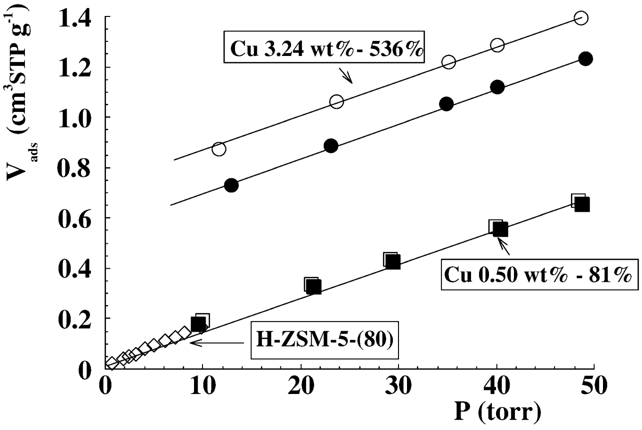

Fig. 4. N_2 adsorption isotherms at 273 K on Cu-ZSM-5 (Si/Al = 80). Two Cu-ZSM-5 samples are reported with copper exchange 81 and 536%. The pure H-ZSM-5 (Si/Al = 80) is reported for comparison. The open symbols are relative to the first adsorption isotherm. The second adsorption isotherm (solid symbols) was measured after evacuation at 7.5×10^{-6} Torr for 30 min at 273 K. The irreversibly adsorbed N_2 is the difference between the first and the second adsorption isotherm at $p = 0$.

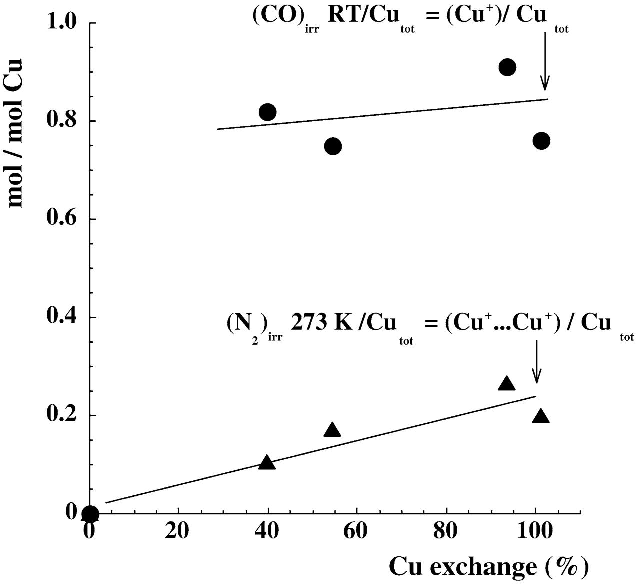

Fig. 5. Self-reduction of Cu(II) species in Cu-ZSM-5 (Si/Al = 25) catalysts after treatment in vacuum at 823 K. The total Cu(I) species titrated by irreversible CO adsorption at room temperature and the special dimeric Cu(I) species able to adsorb irreversibly N_2 at 273 K are reported as a function of the Cu exchange level.

results for Cu-ZSM-5 catalysts (Si/Al = 11.9) and with copper ion-exchange levels from about 10 to 150%, prepared by different methods, including ion-exchange of aqueous solutions of various Cu(II) salts [17a–c], microwave-assisted ion exchange [17d], and chemical vapor deposition [17e]. For the Cu-ZSM-5-(25)-93.6 (Cu 1.78 wt%) sample, the self-reduction process was also followed in a flow microbalance. With a sample mass of 39.40 mg and under a flow of He at 3 ml/min, the weight loss was 0.07 mg in the temperature range of 683–823 K. According to Li and Hall [6], this loss should correspond to the desorption of O_2 formed by self-reduction of Cu(II) species. In fact, 0.07 mg of O_2 corresponds to a fraction of Cu(I) of about 80%, in good agreement with the irreversible adsorption of CO at RT. Fig. 5 shows the results obtained with the same series of samples for the irreversible N_2 adsorption at 273 K, expressed as a $(N_2)_{irr}/Cu_{tot}$ ratio or a $(Cu(I)\cdots Cu(I))/Cu_{tot}$ ratio, assuming that N_2 adsorbs on a dimeric $Cu(I)\cdots Cu(I)$ species. The lower curve in Fig. 5 shows that the N_2 molecule is strongly adsorbed on only a small fraction of the total Cu(I) produced by self-reduction. Such a small fraction of Cu(I) that irreversibly adsorbs N_2 was also reported by Kuroda and coworkers, who pointed out that the most efficient Cu-ZSM-5 catalysts for N_2 adsorption at RT are those prepared by ion exchange of copper acetate solutions [17g].

The catalyst Cu-ZSM-5-(25)-101 (Cu 1.94 wt%) was treated in vacuum at 723, 773, and 823 K; the corresponding $(N_2)_{irr}/Cu$ ratios at 273 K were 0.133, 0.153, and 0.200, indicating that by outgassing at higher temperature a higher fraction of Cu(I) is involved in the irreversible N_2 adsorption at 273 K. For Cu-ZSM-5-(25) preparation the ratio of the irreversible N_2 adsorbed at 273 K over the total amount of copper atoms as a function of copper loading (ranging from diluted to over-exchanged catalysts) is reported in Fig. 6. The TOF for NO decomposition (mole of NO decomposed to N_2 per mole of Cu atoms per second) obtained at 773 K for the same catalysts as a function of the copper loading is reported in Fig. 7.

The data of Figs. 6 and 7 lead to a linear relationship between the TOF and the amount of irreversible N_2 per total copper, as shown in Fig. 8 where the data obtained for

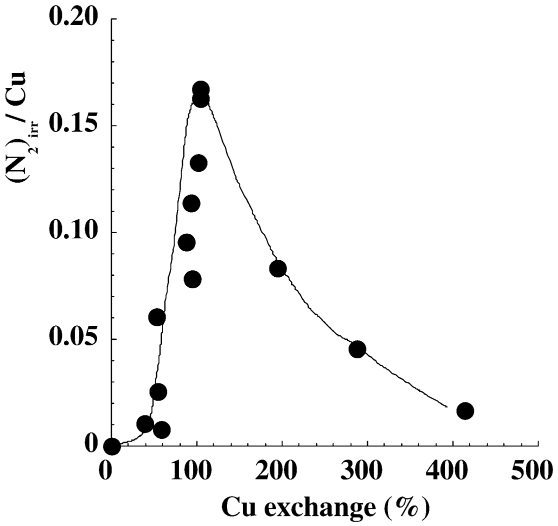

Fig. 6. Amount of irreversible N_2 adsorbed at 273 K per total amount of copper on Cu-ZSM-5 (Si/Al = 25), with copper exchange level ranging from diluted to over-exchanged catalysts. Before the N_2 adsorption, the Cu-ZSM-5 catalysts were treated at 823 K in vacuum.

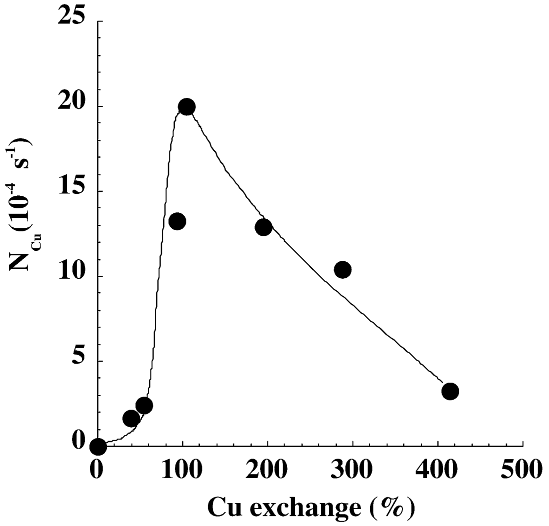

Fig. 7. TOF for NO decomposition on Cu-ZSM-5 (Si/Al = 25) catalysts, with copper exchange level ranging from diluted to over-exchanged catalysts. The NO decomposition was measured at 773 K and with NO 0.46% in He. The TOF was calculated considering the molecules of NO decomposed to N_2 per second per total Cu atoms.

Cu-ZSM-5 (Si/Al = 80) are also reported. The linear relationship strongly supports the view that the active sites for the NO decomposition are the same sites that are able to adsorb N_2 irreversibly at 273 K. It should be noted that the TOF calculated with consideration of only the copper concentration titrated by the irreversible N_2 adsorption is a constant value (about 0.012 s^{-1}, i.e., the slope of the linear relationship in Fig. 8) regardless of the copper loading and of the Si/Al ratio of the ZSM-5 framework.

It is worth noting that the samples Cu-S-1 (MFI framework type without framework Al and Cu 1.38 wt%), Cu-Y (Si/Al = 2.4 with copper exchange 50 and 94%) and Cu-[Al]-MCM41 (Si/Al = 30 with copper exchange 169%) are unable to adsorb N_2 irreversibly at 273 K and are inactive for the NO decomposition under the same experimental conditions as used for Cu-ZSM-5. As a whole, such evidence suggests that dimeric Cu(I) species may be the active sites for NO decomposition on Cu-ZSM-5 catalysts.

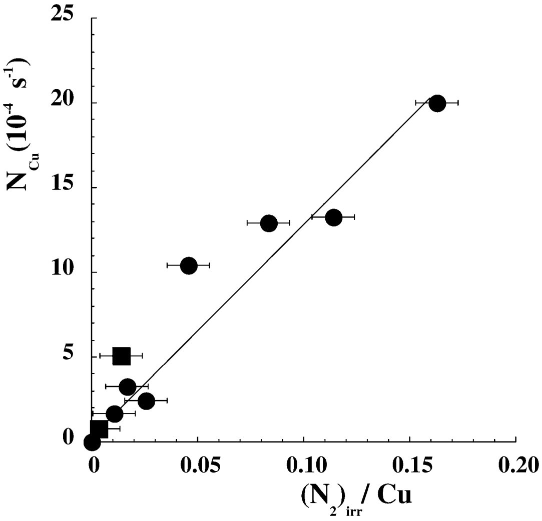

Fig. 8. The data of Figs. 6 and 7 leads to a linear relationship between the TOF and the amount of irreversible N_2 per total Cu atoms on Cu-ZSM-5 (Si/Al = 25). The data obtained on Cu-ZSM-5 (Si/Al = 80) were also included as squares in the plot. The linear relationship gave the value of 0.012 s^{-1} for the true TOF at 773 K and NO 0.5% in He.

DFT calculations were performed to check the experimental results. As reported in Table 1, the calculated interaction energy of N_2 on isolated Cu(I) species is 18.5 kcal mol^{-1} and the intensity of the N≡N stretching is 230 km mol^{-1}. Furthermore, the possible occurrence of Cu(I) couples was considered. When N_2 is coordinated by a pair of Cu(I) ions located on the opposite sides of ten-membered rings in the straight channels of the ZSM-5 framework, along the [010] direction (see Fig. 9), the calculated interaction energy is over 35 kcal mol^{-1}. In this case a μ-η^1:η^1-N_2 (end-on) coordination was obtained, with a quasi-linear Cu–N–N–Cu arrangement and a rather low (27 km mol^{-1}) IR intensity for the N≡N stretching. Such an adsorption mode, never considered before, is of particular interest since it can explain previous results of DRIFT and TPD experiments [15] and may be associated with *irreversibly* adsorbed N_2 at RT. In this respect, we recall that DRIFT spectra of adsorbed N_2 on Cu-ZSM-5 at RT showed *only the reversible* species, with the N≡N stretching band at 2295 cm^{-1}, which disappeared on evacuation at RT [15].

The interaction of O_2 with the Cu(I) ions of the clusters containing one or two Al framework species is also of interest in comparison with the results obtained with N_2. The corresponding computational results are reported in Table 2. The adsorption of N_2 and O_2 on isolated Cu(I) sites is nearly isoenergetic. Among the investigated structures, of particular interest is the one (see Fig. 10) that simulates the interaction of O_2 with two Cu(I) ions placed on the opposite sides

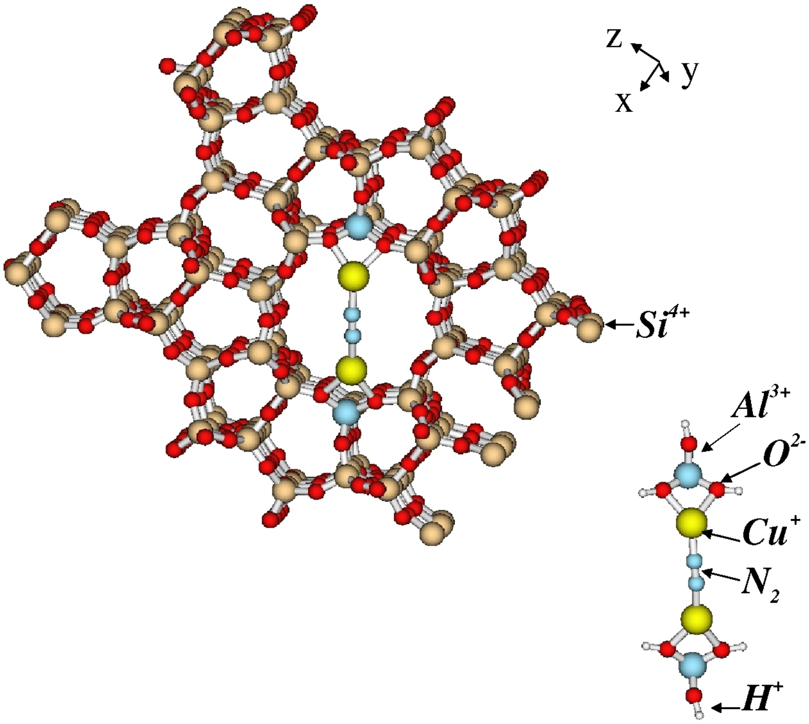

Fig. 9. Graphical model of the irreversible adsorbed μ-η^1:η^1-N_2 (end-on) species between two Cu(I) ions along the straight channels [010] of the ZSM-5 structure. The interaction energy of N_2 with the two Cu(I) ions is -36.5 kcal mol^{-1}, and the Cu(I)···Cu(I) distance is 4.79 Å. The Al···Al, Cu(I)···N and N–N distances are 9.35, 1.86 and 1.10 Å, respectively. (The gas phase N≡N bond length is 1.0975 Å.)

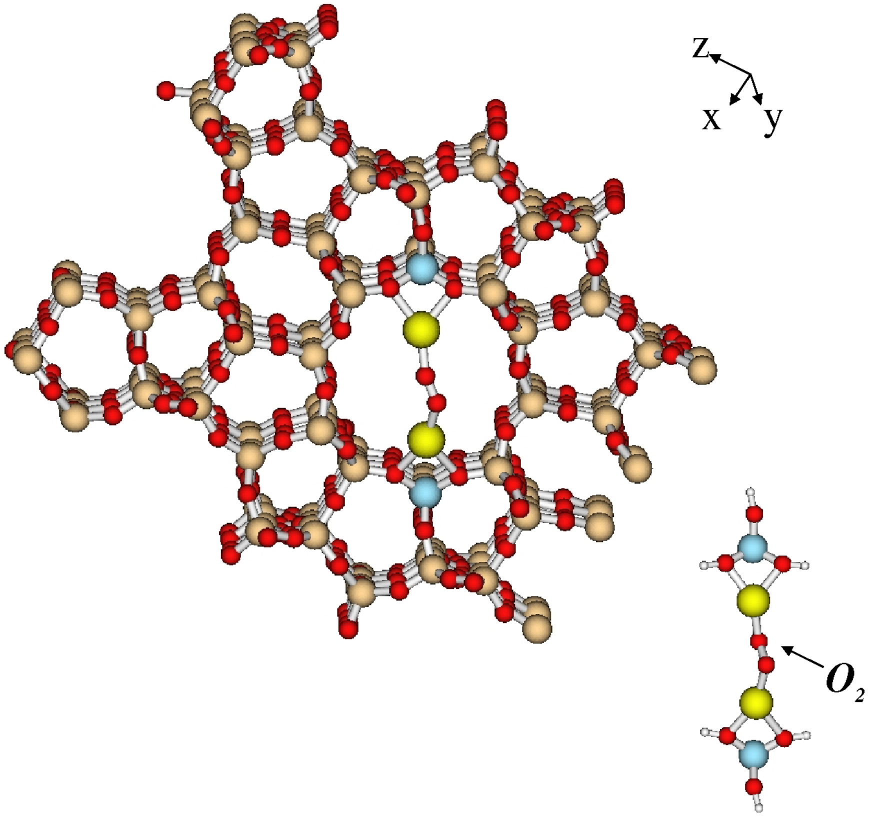

Fig. 10. Graphical model of the *trans*-μ-1,2-O_2 species between two Cu(I) ions along the straight channels [010] of the ZSM-5 structure. The interaction energy of O_2 with the two Cu(I) ions is -83.2 kcal mol^{-1}, and the Cu(I)···Cu(I) distance is 4.83 Å. The Al···Al, Cu(I)···O and O–O distances are 9.35, 1.86 and 1.20 Å, respectively. (The gas phase O=O bond length is 1.208 Å.)

of ten-membered rings along the straight channels of the ZSM-5 framework. The latter structure, designated as *trans*-μ-1,2-O_2, corresponds to the μ-η^1:η^1-N_2 (end-on) geometry (compare Figs. 9 and 10). In this case, the calculated interaction energy is 83.2 kcal mol^{-1}, which is far higher than the interaction energy of N_2 with the same dimeric Cu(I) sites.

4. Discussion

Cu-ZSM-5 is a catalyst that has been much investigated in the last 15 years. Nevertheless, many questions still remain to be answered. It is well established that (i) over-exchanged catalysts are the most active ones [4,6,9,10] and (ii) in vacuum or under inert flowing gas, at high temperature Cu(II) species undergo self-reduction [6,8]. The hypotheses that reduced copper species are the active sites for NO decomposition and that the reaction mechanism proceeds through a redox cycle is widely accepted [7]. The self-reduction of Cu(II) species in Cu-ZSM-5 is a very important step with respect to this point. In fact, the stability and the re-oxidation of Cu(I) sites play a major role in NO decomposition [6,8]. Only Shelef [1] proposed that the reaction entirely proceeds on square-planar Cu(II) sites through the formation of gem-dinitrosyl adsorbed intermediates. The structure of extra-lattice oxygen species (ELO), necessary to balance the charge of the over-exchanged copper species, and the related state of copper between the different oxidation states are highly debated. Sachtler and co-workers [30,31] proposed the existence of bridged O^{2-} ions $(Cu^{2+}–O^{2-}–Cu^{2+})^{2+}$, whereas Bell and co-workers [32,33] hypothesised the presence of ELO species associated with isolated copper sites ($Cu^{2+}–O^-$ and $Cu^{2+}–O_2{}^-$). Consequently, different reaction mechanisms have been proposed. Following the two above possible concepts of ELO identity, at least two major differences could be underlined among the proposed reaction mechanisms. Bell and co-workers [32,33] argued that adjacent pairs of nitrosyl species adsorbed on Cu^+ react to form N_2O, which is subsequently converted to N_2. Giamello et al. [34] and Spoto et al. [35], both proposing the hypothesis that the extra-lattice oxygen species is $Cu^{2+}–O^-$, suggested that the dinitrosyl species are the intermediates in the NO decomposition. The latter conclusion was also supported by Valyon and Hall [36], who noted, however, that under reaction conditions the lifetime of the above species is short and hence their concentration very low. It was also suggested that the mono- and the dinitrosyl are in equilibrium. Although the monomeric nitrosyl is the favoured species at high temperature, the equilibrium would provide a small amount of dinitrosyl not detectable by IR.

In contrast, other groups indicated the importance of NO_2 and of adsorbed nitrate species formation, whose existence could be strictly connected to oxygen bridged ions between copper pairs as key intermediates in the decomposition of NO [37–39].

Valyon and Hall [36] found that the binding energy of O_2 with Cu-ZSM-5 varied in the range from 11 to 54 kcal mol^{-1} as a function of catalyst coverage or catalyst pretreatment temperature. It should be stressed that Hall and co-workers, by using tracer techniques ($^{18}O_2$, $^{15}N\,^{18}O$, $N\,^{18}O$, and $N_2\,^{18}O$) [40], showed that a portion of the catalyst oxygen is mixed into the O_2 released in the NO decomposition and desorbed from Cu-ZSM-5. $N\,^{18}O$ and $N_2\,^{18}O$ undergo exchange with the catalyst oxygen under reaction conditions. In contrast, Chang and McCarty, with the use of isotope-labeled $^{15}N\,^{18}O$ and $^{15}N_2\,^{18}O$ [41], suggested that framework oxygen is not involved in the formation of N_2O from $^{15}N\,^{18}O$, and that the isotope exchange between $^{15}N_2\,^{18}O$ with the zeolite lattice oxygen is not significant.

Previously reported TPD experiments [15] were carried out on Cu-ZSM-5 and H-ZSM-5 exposed to N_2 and then evacuated at 10^{-5} Torr for 30 min. In agreement with our adsorption isotherms, only Cu-ZSM-5 showed a marked N_2 evolution, which started at about 320 K and reached its maximum near 380 K, as revealed by the $m/z = 28$ and $m/z = 14$ mass spectrometry channels. For both systems, no other gaseous products (as revealed by the flat profiles recorded at $m/z = 12, 15, 16, 18, 30, 32$, and 44) were observed, making us confident that N_2 evolution is the only desorption process occurring in this temperature range. However, it is noticeable that Zecchina and co-workers [16] reported that the band at 2295 cm^{-1} related to the formation of $Cu(I)\cdots N_2$ (on top, η^1-N_2) does not completely disappear on a Cu-ZSM-5 catalyst prepared by CVD of CuCl on H-ZSM-5 ($Si/Al = 90$), after the sample is outgassed in vacuo for 4 min at the IR beam temperature. A similar conclusion was reported by Kuroda and co-workers, who pointed out, however, that this is valid for over-exchanged Cu-ZSM-5 ($Si/Al = 11.9$) catalysts prepared by microwave-assisted ion exchange of copper nitrate solutions [17d] or ion exchange of $[Cu(NH_3)_2]^+$ aqueous solution [17f].

On the other hand, DRIFTS experiments [15] showed that the band at 2295 cm^{-1} is observable only under a N_2 atmosphere and completely disappears after an Ar purging (5 min) or a vacuum treatment at RT. This behaviour is completely reversible, as confirmed by a further Ar–N_2 cycle. It appears that the irreversibly adsorbed N_2 is instead IR-silent [15].

Owing to the high local symmetry of the dinitrogen stretching mode, Raman and/or resonance Raman spectroscopies are the only analytical methods available to directly observe the N≡N stretching frequency, and this technique was previously used in a study of bridging N_2 complexes. Two new dinuclear zirconium complexes with a bridging dinitrogen ligand were recently characterised by resonance Raman by Cohen et al. [42]. The N–N equilibrium bond lengths in the complexes are 1.3011(3) Å for the μ-η^1:η^1-N_2 end-on and 1.548(7) for the μ-η^2:η^2-N_2 side-on. However, it should be noted that for most of the metal–dinitrogen complexes the N–N bond lengths are ≈ 1.1 Å; this value is very close to the gas-phase N≡N bond of 1.0975 Å.

Results provided by DFT calculations, summarised in Tables 1 and 2, showed that several geometries are possible for the N_2 and O_2 adsorption on Cu(I) species in the Cu-ZSM-5. However, for energetic reasons, some of them (see Figs. 9 and 10) are more likely to occur. As a comparison, other possible adsorption sites were investigated in the calculations, that is (i) the six-membered ring with mirror symmetry (approximated by an $Al_2Si_2(OH)_{10}Cu_2$–N_2 cluster) along the walls of the linear channels, already considered by Goodman et al. [43b] for O_2 adsorption, and (ii) a linear chain of four or three Si/Al atoms taken along a ten-membered ring of the sinusoidal channel (approximated by the $Al_2Si_2(OH)_{10}Cu_2$–N_2 or $Al_2(OH)_8Cu_2$–N_2 and by the $Al_2Si(OH)_8Cu_2$–N_2 clusters, respectively), already considered by Spuhler et al. [44a] for the location of Cu pairs. As shown in Table 1, in all cases the adsorption of N_2 turned out to be less favourable than that observed between Cu(I) pairs located at the opposite sides of linear channels. It should be noted that Cu(I) is twofold coordinated in all models adopted in the present work, whereas it is known that other kinds of coordination (from three- to fivefold) may occur in Al-substituted ZSM-5 [44a–c]. However, a close inspection of the literature data shows that (i) for a given Al-substituted site, a twofold coordination is often preferred with respect to other kinds of coordination or (ii) when a many-fold coordination is the favoured one, the energy difference with respect to the twofold coordination is generally within a few $\mathrm{kcal\,mol^{-1}}$ [44b]. Taking into account that the twofold Cu(I) coordination is the most favourable one for adsorption, such an energy difference, if any, could easily be compensated for by the interaction energy of the adsorbed species.

Our hypothesis that dimeric Cu(I) sites in Cu-ZSM-5 are the active sites for NO decomposition is also supported by recent literature results. In fact, the presence of the bis-(μ-oxo)dicopper core was identified in O_2 activated over-exchanged Cu-ZSM-5 by UV–vis and EXAFS spectroscopies by Groothaert et al. [45]. The in situ XAFS spectra strongly support the formation of the $[Cu_2\text{-}(\mu\text{-}O)_2]^{2+}$ core during direct NO decomposition. These results suggest the occurrence of a reaction cycle involving the $Cu^+\cdots Cu^+$ pair and the $[Cu_2\text{-}(\mu\text{-}O)_2]^{2+}$ core. Heretofore, the presence of double-O-bridged Cu pairs in Cu-ZSM-5 had only been suggested on the basis of the theoretical study of Goodman et al. [43]. On the other hand, a detailed computational study on the existence of Cu(I) dimers in ZSM-5 was published by Spuhler et al. [44]. In their paper, the geometries and energies of Cu(I) dimers in several sites of ZSM-5 were reported and the clusters proposed here may be considered as possible stable configurations. The results by Groothaert et al. [45] provide experimental evidence of the formation of the bis-(μ-oxo)dicopper core in Cu-ZSM-5 and of its role in the sustained high activity of Cu-ZSM-5 in the direct decomposition of NO into N_2 and O_2. Before these results, the bis-(μ-oxo)dicopper core had only been characterised in synthetic complexes in solution. The latter homogeneous catalysts are able to oxidise selectively organic functional groups and to isomerise to the (μ-η^2:η^2-peroxo)dicopper core, which is the active site in enzymes hemocyanin, tyrosinase, and catechol oxidase. It should also be noted that Groothaert et al. [45b] have shown that, under reaction conditions, the formation of the bis-(μ-oxo)dicopper core in the Cu-ZSM-5 catalysts occurs for a Cu exchange level higher than ca. 40% and that this formation is concomitant with the sharp NO decomposition activity increase. Interestingly, a similar behaviour is shown in Fig. 6, where the amount of irreversible N_2 adsorption is reported as a function of Cu exchange level.

The present results, however, do not support the bis (μ-oxo)dicopper and the (μ-η^2:η^2-peroxo)dicopper coordination. In fact, the distance between the two Cu(I) ions in our model is much larger than that reported by Groothaert et al. [45] (about 2.5–2.7 Å). On the basis of our results, and by taking into account the capacity of the dimeric Cu(I) sites to adsorb N_2 irreversibly at 273 K in a IR-silent way, we propose for the active site the structure shown in Fig. 10. After the evolution of N_2 from two adsorbed NO molecules, the *trans*-μ-1,2-O_2 species left behind, characterised by the strongest interaction energy with the dimeric Cu(I) active site, may be efficiently eliminated only at high temperature, thus explaining the inhibition effect of O_2 for the Cu-ZSM-5 catalyst. With reference to previous work by Goodman et al. [43], where O_2 adsorption by Cu(I) couples coordinated by suitably Al-substituted five- and six-membered rings was considered, the present study shows that O_2 adsorption across the linear channels is energetically more favourable.

Whereas the interaction of N_2 is relatively well characterised by our experimental and the theoretical approaches, the interaction of O_2 with the Cu-ZSM-5 catalyst must be investigated in more detail. An important point that should be further investigated in a specific paper is the influence of the size of the clusters employed in the DFT calculations. In fact, our small clusters require a fixed zeolite framework for the calculations. It may be possible that when relaxation of the framework is allowed, dimeric Cu^+ sites with shorter $Cu^+\cdots Cu^+$ separation are found.

Most of the investigations of the reaction mechanism are based on spectroscopic measurements performed at low temperature, and very rarely have these studies focused attention on the consequent kinetic behaviour of NO decomposition. A power-law rate equation was used to correlate conversion data with NO decomposition rates, but there is no agreement about the dependence on the NO partial pressure, for which an exponent ranging from 0.9 to 1.8 was reported [5–7,10,12].

Transient experiments at low temperature (< 573 K) reported by Pirone et al. [12,46] proved that Cu(I) sites, produced by self-reduction in flowing He at 823 K, are able to convert NO into N_2O until all copper is re-oxidised to Cu(II). At higher temperatures, N_2O is not observable because its rate of decomposition is much faster than the NO decomposition [12,46]. This justifies the absence of the N_2O

decomposition step (over Cu^+ or $Cu^{2+}O^-$ sites) in the kinetic equation of NO decomposition.

A specific and still unexplained aspect of the reaction kinetics is the presence of a reversible maximum of NO conversion to N_2 with increasing reaction temperature (see Fig. 1). Despite significant improvements in the comprehension of the reaction mechanism, the kinetic equation proposed by Li and Hall in 1991 [6] is still used as a reference. However, the rate equation proposed by Li and Hall, which is first order in NO, is neither adequate to describe the overall kinetics from experimental results of integral reactors nor capable of giving a maximum value of NO conversion [46].

On the Cu-ZSM-5 ($Si/Al = 80$) sample studied in this work, the kinetics of NO decomposition was investigated by Pirone et al. [46]. They measured the NO conversion and analysed the distribution of products in different experimental conditions close to those more relevant for practical applications. However, this kinetic study did not deal with the effect of water on the catalyst activity, since the deactivation occurring in the presence of H_2O is so strong that any attempt to investigate reaction kinetics is prevented. A quite large number of kinetic runs were performed, with varying NO and O_2 feed molar fractions, contact time, and temperature. A power-law rate equation showed that the rate order estimated for the NO partial pressure in the temperature range from 673 to 798 K is about 2. The inhibition effect of the O_2 partial pressure results in a negative value for the reaction order of O_2, the absolute value of which decreases slightly from 0.37 to 0.25 with increasing temperature. In the temperature range from 673 to 798 K, no N_2O was detected in the reaction products, as also found in other studies [4,6,10,12,45], whereas NO_2 was produced by the Cu-catalysed reaction between undecomposed NO and the oxygen released from NO decomposition [12]. A rate equation based on a five-step mechanism characterised by the formation of N_2O as key intermediate was obtained by modelling of the conversion data with two competitive reactions (NO oxidation and NO decomposition) occurring in a plug flow reactor [46]. The kinetic model so developed reproduces well the presence of a maximum of NO decomposition rate as a function of the temperature. An intrinsic second-order dependence on the NO partial pressure was found together with an inhibition effect of O_2. The kinetic equation reported by Pirone et al. is based on the following reaction steps:

$$Cu^+ + NO \leftrightarrows [Cu^+NO]$$
(equilibrium step with constant K_{NO}),

$$[Cu^+NO] + NO \rightarrow N_2O + \left[Cu^{2+}O^-\right] \quad \text{(rds)},$$

$$N_2O + Cu^+ \rightarrow \left[Cu^{2+}O^-\right] + N_2 \quad \text{(very fast)},$$

$$N_2O + \left[Cu^{2+}O^-\right] \rightarrow N_2 + O_2 + Cu^+ \quad \text{(very fast)},$$

$$2\left[Cu^{2+}O^-\right] \leftrightarrows O_2 + 2Cu^+$$
(equilibrium step with constant $1/K_{O_2}$).

The kinetic equation obtained by taking into account the proposed rate determining step (rds), the equilibrium steps, and the balance of Cu^+ species involved in the steps is the following:

$$r = k[Cu^+]_{tot} K_{NO} p_{NO}^2 / (1 + K_{O_2}^{1/2} p_{O_2}^{1/2} + K_{NO} p_{NO}).$$

Pirone et al. estimated the parameter k, K_{NO}, and K_{O_2} by fitting the experimental data and using a derivative-free minimisation algorithm. The activation energy of 25.7 $kcal\,mol^{-1}$ was estimated with the kinetic constant k relative to the rds. The adsorption heat of NO on Cu-ZSM-5 was evaluated by analysis of the dependence of K_{NO} on temperature. The value was -58.3 $kcal\,mol^{-1}$, in good agreement with the DFT calculation reported by Trout et al. [32], who gave values in the range between -42.8 and -77.7 $kcal\,mol^{-1}$. The adsorption heat of O_2 obtained by analysis of the dependence of K_{O_2} on temperature was equal to -43.6 $kcal\,mol^{-1}$.

The overall reaction rate does not monotonously increase with temperature, and above 773 K the activation energy becomes negative (see Fig. 1). According to the kinetic model, the factor $kK_{NO}[Cu^+]_{tot}$ is proportional to $\exp[-(E_a + \Delta H_{NO})]/RT$ and is equal to $\exp(32.6/RT)$. At lower temperatures, the denominator of the kinetic equation reported above becomes $(1 + K_{O_2}^{1/2} p_{O_2}^{1/2} + K_{NO} p_{NO}) \approx K_{NO} p_{NO} = p_{NO} \exp(58.3/RT)$, and the rate increases with increasing temperature. At higher temperature, $(1 + K_{O_2}^{1/2} p_{O_2}^{1/2} + K_{NO} p_{NO}) \approx 1$, the rate decreases when the temperature increases.

On the basis of our experimental findings, the rds and the step involving the release of O_2 from the catalyst surface should be written as

$$(Cu^+)_2\,NO + NO \rightarrow N_2 + (Cu^+)_2O_2 \quad \text{(rds)},$$

$$(Cu^+)_2O_2 \leftrightarrows O_2 + (Cu^+)_2.$$

These two steps are in agreement with the intrinsic second-order dependence on the NO partial pressure and the inhibition effect of O_2. Moreover, the concentration of Cu(I) pairs should increase with increasing Al content of the ZSM-5 unit cell, as was shown in a former study [11]. The dimeric Cu(I) sites can be titrated by irreversible N_2 adsorption at 273 K. As suggested by DRIFT results and DFT calculations, such pairs of Cu(I) ions may be located at two opposite sites of the ten-membered oxygen rings along the linear channels of the ZSM-5 zeolite.

A further point to discuss is related to the probability of finding two framework Al in the ZSM-5 structure at the opposite sites of the ten-membered oxygen ring along the [010] straight channels. As Ricchiardi and Newsam suggested, on the basis of a classical mechanical method, quite similar energies are expected for the substitution of Al into the different T-sites of the ZSM-5 framework [47]. If this is correct, the concentration of the *favourable* dimeric Cu(I) pairs should be strongly limited by the Si/Al atomic ratio of the framework. However, zeolites are metastable materials crystallised hydrothermally under kinetic control, and even if the relative T-site substitution energies for the different sites are similar, the actual aluminum distributions in real materials may be determined by the particular synthesis conditions. As a consequence, two framework Al in the ZSM-5 structure at the opposite sites of the ten-membered oxygen ring along the [010] straight channels may be, for kinetic reasons, an eventuality more common than expected.

5. Conclusions

The present work confirms the unique capacity of Cu-ZSM-5 catalysts to adsorb N_2 irreversibly at low temperature (273–325 K). The adsorbed species are actually stable up to about 400 K under dynamic TPD experiments. The adsorbed species are IR-silent, suggesting a rather symmetric Cu(I)–N_2–Cu(I) geometry. An appropriate model for this kind of adsorption was successfully tested by means of DFT calculations. When the TOF for the NO decomposition was calculated, with the use of only the copper concentration titrated by the irreversible N_2 adsorption at low temperature, a constant value was obtained independently of the copper loading and of the Si/Al ratio of the ZSM-5 zeolite. This could answer a long-debated question about the unusual sigmoidal relationship between the TOF and the copper loading.

It is clear that more active catalysts can be developed when more is learned about Cu-ZSM-5, particularly about the oxygen desorption step from the active site. For a practical application, the new NO decomposition catalysts should be stable in the presence of water and active at a temperature well below 773 K. As recently discussed by Goralski and Schneider [48], according to LEV-II and Tier II NO_x emission standards, the lean-burn NO_x control for automobiles based on the idea of NO decomposition would need a catalyst with 100% activity at temperatures as low as 423 K.

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