Effects of the Si / Al atomic ratio on the activity of Cu-ZSM-5 catalysts for nitric oxide decomposition

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A review of literature data for nitric oxide decomposition over Cu-ZSM-5 catalysts leads us to conclude that the turnover frequency depends on the Si / Al atomic ratio in a way opposite to the trend suggested by Iwamoto and co-workers and considered correct by Shelef in a recent letter published in this journal. In particular we show that the turnover frequency increases with the number of Al atoms per unit cell (i.e. decreasing the Si / Al atomic ratio). This result suggests that the most active sites for NO decomposition over Cu-ZSM-5 catalysts may contain two close copper ions.

Keywords: NO decomposition; Cu-ZSM-5

1. Introduction

In a recent letter published in this journal Shelef [1]proposed a mechanism for NO decomposition over Cu-ZSM-5 involving coordinatively unsaturated Cu^{2+} sites in a square planar configuration on which two NO molecules are chemisorbed in the gem-dinitrosyl form. At the reaction temperature this complex is supposed to decompose into nitrogen and oxygen without involving a redox process. Shelef has shown that his conclusions are consistent with the salient characteristics of NO decomposition on Cu-ZSM-5 described by Iwamoto and co-workers [2,3] and Li and Hall [5,6].

Hall and Valyon [7–9] have summarized the evidence favoring redox chemistry but have pointed out conditions under which Shelef could be correct. Hall and Valyon presented new data showing the IR spectra of surface species recorded under in situ reaction conditions. They showed that the dinitrosyl bands were too weak to characterize. At the same time they showed the presence of bands corresponding to chemisorbed NO_2 and probably to mono- and bimolecular complexes of NO_2 and NO with NO_2. Hall and Valyon concluded that if these species are the true reaction intermediates Shelef could be correct.

Shelef [1] and Hall and Valyon [7] in their reviews of literature results considered correct the conclusion reported by Iwamoto and co-workers [2,3] about the influence of the Si/Al ratio on the specific decomposition rate per exchanged copper. These authors reported that the catalytic activity per site increases with the Si/Al ratio. Shelef [1] remarked: "Pairing of nitrogens by the interaction of two NO species, each one adsorbed on a different copper site does not seem probable because in high-silica zeolites the copper ions are spaced too far apart." A similar conclusion was expressed by Hall and Valyon [7]: "Yet Iwamoto's data shows the catalytic activity per site increases with the Si/Al ratio. We, on the other hand, have suggested that the reaction occurs on single Cu^+ sites by forming first the mononitrosyl, then the gem-dinitrosyl which decomposes into N_2O leaving an oxygen behind."

In this letter, by means of a review of recent literature data, we consider again the effect of the Si/Al ratio on the catalytic activity per site and arrive at a conclusion opposite to that reported by Iwamoto and co-workers [2,3]. This result suggests that on the most active catalysts (lower Si/Al ratio, high copper loading) the proposed mechanism of NO decomposition, involving a redox process (Iwamoto–Hall mechanism) or not (Shelef mechanism), should involve sites consisting of two close copper ions.

2. Review of literature data

In table 1 we report literature data on the catalytic decomposition of NO over Cu-ZSM-5 catalysts obtained in the differential region at 773 K and normalized to

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 1.0 [6]. N_{Cu} is the turnover frequency of NO decomposition expressed as twice the number of N_2 molecules produced per Cu ion per second; 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 expressed as twice the number of N_2 molecules produced per copper atom 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

Si/Al	p/Al per u.c.	Cu (wt%)	% of exchange	$R_g \times 10^{-17}$	$N_{Cu} \times 10^3$	Ref.
11.7	7.56	5.69	152	75.4	14.0	[4]
12.3	7.22	5.04	140	69.7	14.1	[6]
14	6.40	3.12	96	30.9	10.1	[6]
21	4.36	2.54	114	27.1	10.7	[6]
23	4.00	2.06	100	2.49	1.31	[11]
24.2	3.81	1.50	76	8.33	2.83	[6]
26.4	3.50	2.96	166	19.6	6.65	[6]
27	3.43	0.89	50	5.74	6.05	[10]
Cu/SiO_2	(0.00)	0.86	–	0.0164	0.02	[12]

NO 4% of an atmosphere assuming, according to Li and Hall [6], a reaction order in NO equal to 1.0. Details about the Cu-ZSM-5 catalysts, i.e. Si/Al atomic ratio and number of Al atoms per u.c., are also reported in table 1.

We recall that Iwamoto and co-workers [2,3] 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 of ref. [2]). This result was based on data obtained at 673 K and with a reaction mixture NO 4% in He. Iwamoto and co-workers studied catalysts at 40–50% exchange levels (100% corresponds to 1 Cu^{2+} per 2 Al atoms) to keep conversions low and to treat the system as a differential reactor. No details about the exact level of conversions were reported by Iwamoto and co-workers, nevertheless the suggested linear trend was considered correct (also for catalysts with higher copper loadings) by Shelef [1] and Hall and co-workers [5–9].

Recently Li and Hall [6] and Iwamoto et al. [4] reported new kinetic data obtained under a true differential regime, i.e. the conversions were kept below 10% to ensure the reaction rates were not diffusion limited. These new data together with others obtained by Sepùlveda-Escribano et al. [10], and Guczi and Schay [11] are also reported in table 1. All the catalysts, with the exception of the catalyst studied by Guczi and Schay, were prepared by ion-exchange in an aqueous Cu(II) acetate or nitrate solution. Guczi and Schay prepared their catalyst by solid state ion-exchange of H-ZSM-5 by $CuCl_2$ at 800 K obtaining an exchange of 50% of the H^+ sites with $CuCl^+$ species [11].

For comparison in table 1 we also report the result obtained by Hamada et al. [12] on the catalysts Cu/SiO_2 prepared by ion-exchange of silica with an aqueous Cu(II) acetate solution.

It should be noted that the data reported by Li and Hall in table 2 of ref. [6] must be divided by a factor 2. This is because, as shown in their fig. 1 and commented on p. 204 of ref. [6], the slope of the plots "Conversion to Nitrogen % vs. W/F in g s/mmol NO", represents already the rate in millimoles of NO converted to N_2 per gram of catalyst per second and it is not necessary to multiply this number by 2. This correction leads to a very good agreement between the results obtained by Li and Hall [6] and Iwamoto et al. [4] on catalysts with similar Si/Al ratio ($\sim$ 12), as shown in our table 1. Also the data obtained from refs. [10,11] deserve further comments. Sepùlveda-Escribano et al. [10] reported the rate as total number of NO molecules converted per gram of catalyst per second. According to a personal communication by J.L.G. Fierro the rates reported in fig. 5 of ref. [10] must be divided by a factor 100; at 773 K and 3% NO/He the total rate was 1.43 μmol/g s. It is well known that the true rate of the decomposition reaction is the rate of N_2 production, i.e. the rate of conversion of NO to N_2. This datum is lacking and therefore we considered that at low conversion and at 773 K ($[O_2] \approx 0$) the concentration of N_2O is very low so that the true decomposition rate can be approximate to 1/2 the total rate of NO conversion (conv. $N_2 \approx \frac{1}{2}$ conv. NO). Also the data reported by Guczi and Schay [11] did not consider the number of N_2 molecules formed but only the total number of NO molecules converted and therefore similar approximations as discussed above were necessary. It should be stressed that the data from refs. [10,11] lead to a maximum value for the rate of the true NO decomposition.

The analysis of these new results leads to conclusions opposite to that previously reported by Iwamoto and co-workers and recently commented by Shelef [1] and Hall and Valyon [7].

In fig. 1 we show a plot of the activity per gram of Cu-ZSM-5 catalysts, expressed as twice the number of N_2 molecules produced per gram of catalyst per second (R_g), as a function of copper loading in wt%. Each data corresponds to a ZSM-5 zeolite containing p Al atoms per unit cell and to a certain per cent of exchange (see table 1 for details). Note that for most of the catalysts the exchange levels are close to or higher than 100%. The rates obtained at exchange levels less than 100% could increase at exchange levels close to or higher than 100%. We recall that if all Cu ions are considered active sites the turnover frequency N_{Cu} can be easily obtained from R_g:

$$N_{Cu} = R_g \times 100 \times 63.54/(\text{Cu wt\%}) \times 6.023 \times 10^{23}\,.$$

The results in fig. 1 clearly show the N_{Cu} increases with the number of Al atoms per u.c. of the ZSM-5 zeolite, i.e. decreasing the Si/Al ratio. A plot of R_g versus p shows a similar trend to that reported in fig. 1 while a plot of R_g versus p^2 shows to good approximation a linear correlation, suggesting that two close copper ions could be the active sites for the NO decomposition in Cu-ZSM-5 catalysts at high

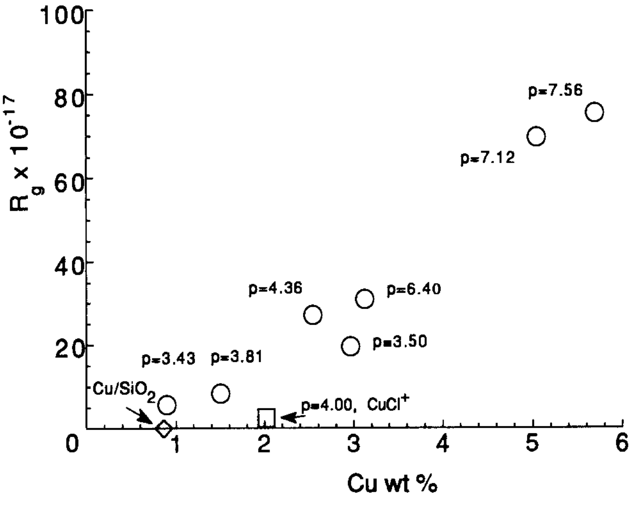

Fig. 1. Activity per gram of Cu-ZSM-5 catalysts R_g, expressed as twice the number of N_2 molecules produced per gram of catalyst per second, as a function of copper loading in wt%. Each datum corresponds to a ZSM-5 zeolite containing p Al atoms per unit cell and to a certain % of exchange (see table 1 for details). Note that for most of the catalysts the exchange levels are close to or higher than 100%. The rates obtained at exchange levels less than 100% could increase at exchange levels close to or higher than 100%.

copper loadings. The trend in fig. 1 is opposite to that reported by Iwamoto and co-workers [2,3]. To explain this contradiction we tentatively suggest that Iwamoto and co-workers may be correct only at low copper loadings (i.e. exchange levels $\leqslant 50\%$). (However we think that new kinetic data obtained in the differential region on Cu-ZSM-5 catalysts at low copper loadings are necessary to confirm this hypothesis.)

A comparison of the data shown in fig. 1 and reported in table 1 demonstrates that the catalyst prepared by solid state ion-exchange and containing $CuCl^+$ species is less active with respect to the other catalysts with similar Si/Al ratios and prepared by ion-exchange in solution. The Cu/SiO_2 catalyst is practically inactive and this confirms the importance of the unique electronic and geometrical structure of the copper sites in Cu-ZSM-5.

We may add that the most active 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 [9,13]. This influence has been attributed to the formation of catalytically active metal oxygen bridge species within the zeolite cavities (i.e. M^{n+}–O^{2-}–M^{n+} species where the anion corresponds to extralattice oxide ions) [9,13]. The formation of such species would be expected to be favored by high metal loadings and hydrolysis conditions during ion exchange, as is observed experimentally [9,13].

3. Final remark

A review of literature data shows that the turnover frequency for NO decomposition over Cu-ZSM-5 catalysts increases with the number of Al atoms per unit cell of ZSM-5 (i.e. decreasing the Si/Al ratio). This trend is opposite to the one previously reported by Iwamoto and co-workers [2,3]. This suggests that in the most active catalysts (Cu-ZSM-5 catalysts with the lower Si/Al ratios) the active sites 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. According to Hall and co-workers [6–9] and Shelef [1] two NO molecules adsorbed on a single copper ion (Cu^{2+} or Cu^+) in the gem-dinitrosyl form could decompose into nitrogen and oxygen. We note that 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 per u.c., and high copper loadings) may consist of two close copper ions.

Due to the fact that the zeolites ZSM-5 cannot be prepared with Si/Al ratios lower than about 11 [14], on the basis of fig. 1 we conclude that a practical catalyst for NO decomposition (one or two orders of magnitude more active than the best Cu-ZSM-5 catalysts [1]) could be obtained only considering modified versions of the Cu-ZSM-5 catalyst or, of course, with the discovery of a new type of catalyst.

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