Transient behaviour of Cu-overexchanged ZSM-5 catalyst in NO decomposition

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The adsorption of NO at 80°C on Cu-overexchanged ZSM-5 ($Si/Al = 80$) has been investigated in a flow apparatus. The formation of N_2O during a transient phase was observed after He pretreatment of the zeolite at 550°C. A negligible amount of N_2O was detected, in contrast, from O_2 pretreated zeolite. The formation of N_2O has been associated to the reoxidation from Cu^+ to Cu^{2+} of a fraction (about 40%) of copper in the zeolite. The redox chemistry in NO adsorption at low temperature can be related to the activity of Cu-ZSM-5 zeolite in NO decomposition.

Keywords: unsteady-state adsorption, NO adsorption, Cu-ZSM-5, overexchange, redox properties

1. Introduction

The technologies for the abatement of nitrogen oxides (NO_x) generated as by-products of high-temperature combustion processes, are based on their selective catalytic reduction (NO_x SCR), either from mobile [1] or from fixed sources [2]. The catalytic decomposition of NO_x to elements is very attractive in principle as it does not require any reductant and is strongly favoured by thermodynamics at temperatures lower than 800°C. Nevertheless, low catalytic performance due to kinetic limitations had been achieved until recently [3].

Renewed interest for the catalytic decomposition of NO_x was originated by the discovery by Iwamoto and co-workers [4] of the high activity of Cu-ZSM-5 zeolite. A very large number of papers have been published on this subject, as recently reviewed [5–7]. It was reported that overexchanging Cu-ZSM-5 to $Cu/Al > 0.5$ (up to 166% exchange) resulted in higher activity per Cu ion in NO decomposition with respect to the underexchanged samples [8–10]. We have found that copper overexchanging of H-ZSM-5 with $Si/Al = 80$ is very easy to be performed up to 650% exchange, without any evidence for the presence of bulk copper oxide species [11]. The turnover frequency of NO decomposition over these catalysts increases with the copper loading with a maximum value at about 500% overexchange [12], giving further evidence of very high dispersion of copper within the zeolite [11,13].

The nature of the overexchanged copper was investigated in many papers [8,14–17]. By experiments of isopropylammine adsorption–desorption performed on Cu-ZSM-5, Parrillo [15] concluded that the exchange stoichiometry was not the usually assumed (one Cu for two Al) and suggested that not all the copper could be associated to the Al sites. No assured explanation for the overexchange phenomenon still exists, but the possibility that the exchanging cation in the zeolite is $[Cu(OH)]^+$ and its related oligomers, instead of Cu^{2+}, has been also suggested [16,17].

It has been proposed that copper sites in Cu-ZSM-5 could be easily reduced (from Cu^{2+} to Cu^+) by only raising the temperature above 400°C, due to spontaneous desorption of oxygen. It has been also reported that NO is easily adsorbed on both Cu^{2+} and Cu^+ sites [18–20], but that only NO adsorbed on the reduced copper is able to generate the decomposition products. The process is effective above 400°C, since at lower temperatures the oxygen produced by the reaction cannot be desorbed and the reduced state of the catalyst is not restored. Consequently, it has been proposed that the NO decomposition proceeds over Cu-ZSM-5 by a redox mechanism [4,9,21] in which Cu^+ ions are active centres and the catalytic cycle is closed by oxygen desorption at high temperature [21–24]. Iwamoto [9] proposed a mechanism involving coupled copper ions and Moretti [28] assumed single Cu or $[Cu–O–Cu]^{2+}$ ions as catalytic sites, with a turnover frequency much higher for the latter. In contrast, Shelef [29] proposed a mechanism which does not require a surface redox process, pointing out the importance of NO_2 as intermediate for the reduction to N_2 [30]. The importance of $Cu^{2+}O^-$ as active site has been also proposed [31].

Investigations of the interactions between NO and Cu-ZSM-5 should contribute to the elucidation of the mechanism of NO decomposition. During adsorption at 25°C no catalytic reaction of NO was detected by Iwamoto and co-workers [4,9] in the steady state, whereas the appearance of N_2O and N_2 in the gas phase was reported by Li and Armor [26]. The formation of a complex such as N_2O_3 with a Cu ion within the zeolite after co-adsorption of NO and NO_2 was suggested in ref. [22]. The interaction of NO with Cu-ZSM-5 was also investigated by TPD [22,26,32–35]. Only two NO desorption peaks were reported in refs. [22,32,33,35]; several NO peaks together with N_2O and O_2 peaks in refs. [26,34]. Other authors reported that NO oxidized Cu^+ to Cu^{2+} even at room temperature with release of N_2 [4,21,25–27].

In the present study the unsteady-state behaviour at low temperature of overexchanged Cu-ZSM-5 has been utilised to clarify the changes of copper oxidation state.

2. Experimental

Overexchanged Cu-ZSM-5 was prepared by performing ion exchange of H-ZSM-5 zeolite (Si/Al = 80) with copper acetate aqueous solution for 2 h at 50°C and subsequent drying at 110°C [11]. The catalyst, labelled as Cu-ZSM-5(640), has 3.94 wt% Cu content, corresponding to about 640% overexchange, 100% exchange corresponding to the atomic ratio $Cu/Al = 0.5$ (0.62 Cu wt%).

A fixed-bed microreactor consisting of a 60 cm long quartz tube (i.d. 1.0 cm), in which a porous disk supports the catalyst particles, was used to perform the experiments. The reactor was inserted in a furnace supplied with three heated and temperature controlled zones. The temperature of the catalytic bed was measured by a chromel–alumel thermocouple, placed in a quartz tube, coaxial and internal to the reactor. Three Brooks mass flow controllers were used to measure the flow rates of high purity gases: NO (1 vol%) + He, He (99.995%) and O_2 (99.995%). Before each experiment, the catalyst was treated in He (25 Nℓ/h) for 2 h at 550°C in order to obtain the reduced state (r.s.) or in O_2 overnight to obtain the oxidized state (o.s.) and then quenched down to the desired temperature, respectively in He or O_2 flow ($\sim$ 1 Nℓ/h). In a typical experiment NO (600 ppm in volume) and He were fed to the reactor at a temperature as low as the catalyst exhibited no steady-state activity in NO decomposition. The transient behaviour of the system was registered by analyzing the inlet and the outlet reactor gas with Hartmann and Braunn continuous analyzers for NO, NO_2 and N_2O (URAS 10 E and RADAS 1G), and with a Hewlett Packard HP 5890 gas-chromatograph (MS 5A column) for N_2 and O_2.

3. Results

The reaction rates previously reported [12] for the catalytic decomposition of NO on Cu-ZSM-5, measured under steady-state conditions, were not affected by the initial state (r.s. or o.s.) of the catalyst. On the contrary, the pretreatment strongly influenced the catalyst performance before reaching the steady-state conversion. This is shown in fig. 1, where typical patterns of NO outlet concentrations as functions of time in two different runs, carried out at 500°C respectively on r.s. and o.s. Cu-ZSM5(640), are reported. It appears that the steady-state outlet concentration of NO is the same (3835 ppm) for both experiments, but in the whole transient is lower on r.s. and higher on o.s. catalyst. It is likely that the final state of oxidation of the catalyst is intermediate between the most oxidized (and less active) and the most reduced (and more active) one. In order to investigate the redox

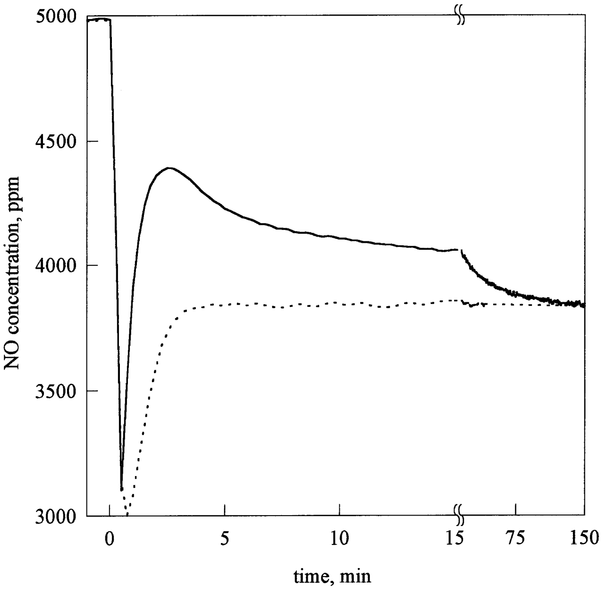

Fig. 1. Outlet reactor concentration of NO against time in two runs of catalytic decomposition on r.s. (...) or o.s. (——) Cu-ZSM-5(640) ($T = 500$°C, NO inlet concentration = 5000 ppm).

chemistry of Cu-ZSM-5 and its interaction with NO a transient analysis of the dynamic behaviour of the NO/catalyst system was carried out.

Fig. 2a shows the typical pattern of NO and N_2O outlet concentrations after a step change of NO concentration in the feed (from 0 to 600 ppm) to r.s. Cu-ZSM-5(640). At 80°C, the catalyst has no steady-state activity in reactions involving NO, as previously shown [12].

The steady-state NO outlet concentration reached the inlet value in about half a day through two distinct steps. In the first step, no nitrogen-containing species nor O_2 were detected in the outlet reactor for about 20 min, whereas in the second step the catalyst released N_2O and NO. No transient formation of N_2 was observed during the whole experiment, differently with findings of Li and Armor [26] and Iwamoto [9] in similar experiments carried out at room temperature on a lower Si/Al ratio Cu-ZSM5. However, the first phase of the transient suggests that during this time NO was adsorbing on the catalyst. In the second step, the outlet concentration of N_2O rapidly increased up to a maximum value of about 300 ppm after 25 min from the beginning of the experiment and then decreased much more slowly, becoming negligible only after about 12 h. Instead, NO was not detected in the first 25 min, i.e. up to the time corresponding to the maximum of N_2O outlet concentration. After this time, the NO concentration increased in 10 min up to 450 ppm, but took much more time to reach the steady-state value of 600 ppm.

The calculation of the total amount of NO consumed and N_2O produced in the transient phase indicates that N_2O formation (1.3×10^{-4} mol/g) is not sufficient to explain the corresponding consumption of NO occurring during the whole run time (4.9×10^{-4} mol/g), being smaller than half the amount of NO fed. Consequently, the material balance for the nitrogen-containing species can be closed only by taking into account that a substantial amount of NO remains adsorbed on the catalyst, equal to the difference between the total NO consumption and twice the N_2O production in the whole experiment. It is worthwhile to notice that, O_2 not being detected in the reaction products during the whole experiment, neither the material balance of oxygen was closed with NO and N_2O measured in the outlet gas and NO adsorbed on catalyst. Consequently, the possibility that a significant amount of oxygen remains on the Cu-ZSM-5 surface is to be taken into account, too. In particular, it can be assumed that NO is able to reoxidize copper sites of the zeolite, according to the stoichiometry reported below:

$$2NO + 2Cu^{+} \rightarrow N_2O + (Cu{-}O{-}Cu)^{2+} \qquad (1)$$

Similar conclusions were also reported by Giamello et al. [18] and Lei et al. [16] from experimental results of EPR and IR spectroscopy.

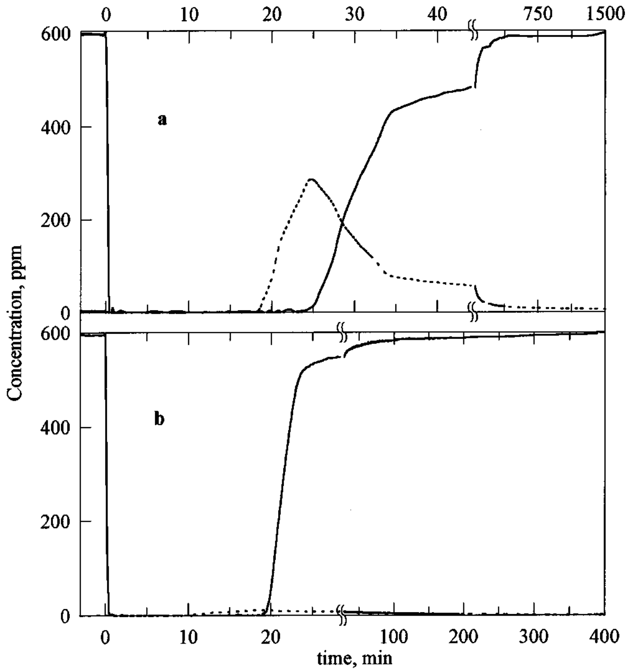

Fig. 2. Outlet gas concentration of NO (——) and N_2O (...) against time in NO adsorption run on: (a) r.s., (b) o.s. Cu-ZSM-5(640) ($T = 80°C$, NO inlet gas concentration = 600 ppm).

All the observed phenomena are associated to the presence of copper in the zeolite. In fact, by carrying out the same adsorption experiment on the parent zeolite, H-ZSM-5, no N_2O was observed in the transient time, whereas the amount of NO adsorbed was 6.3×10^{-6} mol/g, quite negligible with respect to that found on the Cu-exchanged sample.

The above assumptions on the material balances on nitrogen- and oxygen-containing molecules were also confirmed by a series of experimental validations. The amount of nitric oxide adsorbed during the unsteady state of the experiment of fig. 2a was measured by thermal desorption (TPD) performed at the end of that run. In the TPD test (fig. 3), only NO and O_2 were desorbed from the catalyst, in agreement with similar reported results [32,33,35]. Three different peaks of NO concentration were detected in the products. The total amount of desorbed NO (2.1×10^{-4} mol/g) is very similar to the amount of NO irreversibly adsorbed in the transient experiment of fig. 2a (2.3×10^{-4} mol/g), and then allows the nitrogen balance to be closed within 5% error.

Carrying out the same experiment as that of fig. 2a on the o.s. catalyst, we have found (fig. 2b) that the pretreatment in O_2 resulted in a very strong decrease of the amount of N_2O desorbed (5.9×10^{-6} mol/g) with respect to that obtained from the r.s. catalyst. By assuming that the catalyst was in the highest oxidation state upon O_2 pretreatment, we conclude that the formation of N_2O must be associated to copper reoxidation in the zeolite.

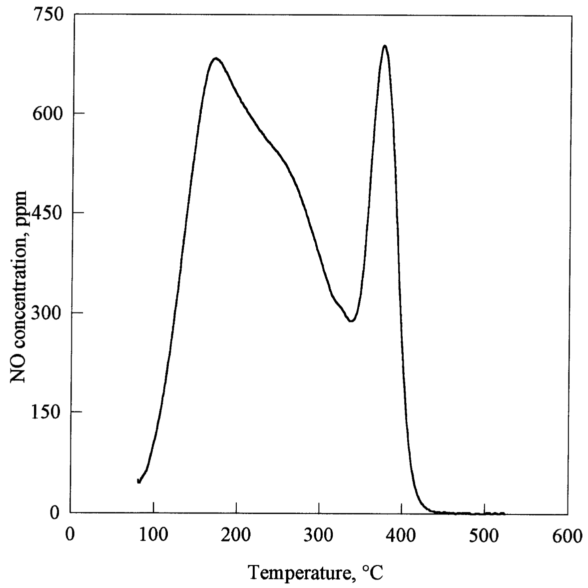

Fig. 3. Gas concentration of NO in TPD test performed after adsorption run of fig. 2a. Heating rate, 9°C/min; He flow rate, 25 Nℓ/h.

In contrast to what has been found for the formation of N_2O, the amount of adsorbed NO is not dependent on catalyst pretreatment, being 2.0×10^{-4} mol/g for the o.s. catalyst. Then, the same fraction of copper (3–4 Cu atoms per NO molecule) seems to be involved in NO adsorption.

Since the observed effects should be attributed to the reduction of the catalyst, we have measured the O_2 concentration in the outlet gas during the He treatment at 550°C. Two main peaks (fig. 4) were detected, in agreement with findings in refs. [23,35]. Specifically, the first peak appeared at about 350°C, in correspondence to the third desorption peak of NO in the TPD experiment (fig. 3), in good agreement with the experimental results reported in refs. [26,33–35]; the second peak at higher temperatures (> 500°C), as found in refs. [23,35]. The total amount of O_2 desorbed from the catalyst (6.2×10^{-5} mol/g) is about 50% the amount of N_2O measured in the transient experiment of fig. 2a. This result strongly supports the assumption that copper sites reduced upon He treatment at 500°C are reoxidised during the transient adsorption of NO.

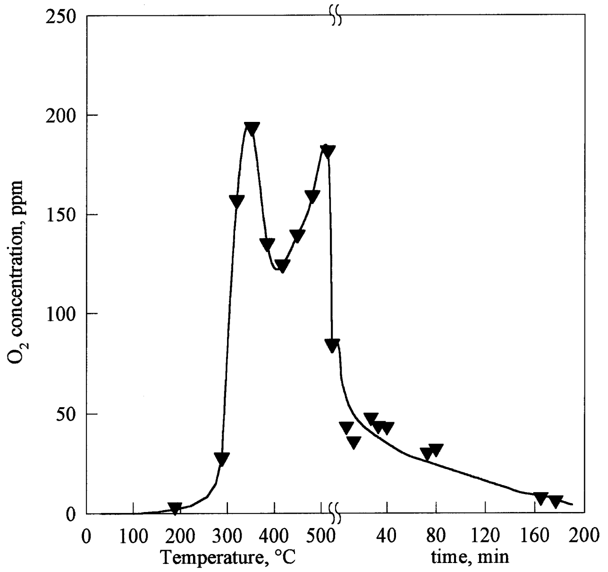

Fig. 4. O_2 TPD during He pretreatment of Cu-ZSM-5(640). Heating rate, 5°C/min; He flow rate, 5 Nℓ/h.

4. Discussion

Our experimental results of NO adsorption at low temperature have shown that this technique succeeds in *titrating* copper sites which undergo the self-reduction from Cu^{2+} to Cu^{+}, by desorbing molecular O_2 above 350°C. These sites are probably involved in NO decomposition, if a redox mechanism is assumed.

During the reducing pretreatment of catalyst in flowing He at 550°C, the redox stoichiometry for copper sites is:

$$4Cu^{2+} + 4e^{-} \rightarrow 4Cu^{+} \tag{2a}$$

$$2O^{2-} \rightarrow O_2 + 4e^{-} \tag{2b}$$

It is evident that the formation of one gas molecule of O_2 should be associated to the reduction of four Cu^{2+}, but the high atomic distance among Al sites in the zeolite (about 1 Al per unit cell) makes the probability of this event very low, if the exchanged copper is only associated to the Al ions according to the usually assumed ion-exchange stoichiometry (1 Cu for 2 Al). Since the molar ratio of [Cu]/[Al] in Cu-ZSM-5(640) is around 3.2 and no presence of bulk copper oxide species was observed [11], a different exchange stoichiometry could be hypothesized. The presence of $[Cu(OH)]^{+}$ species and their related oligomers such as $[Cu_xO_2(OH)_{2x-5}]^{+}$ instead of Cu^{2+} as exchanging cations in Cu-ZSM-5 has been already suggested [14,16–17]. Such species could explain both the copper overexchange and the self-reduction in ZSM-5 zeolite with Si/Al ratio as high as 80. In fact, for $x \geqslant 4$, the very low distances among Cu atoms, all associated to the same Al site, allows the thermal self-reduction to occur. For example, for $x = 4$, the stoichiometry of catalyst self-reduction is

$$[Cu_4O_2(OH)_3]^{+} \rightarrow [Cu_4(OH)_3]^{+} + O_2 \tag{3}$$

According to the scheme (3) and the stoichiometry ((2a) and (2b)), only the copper atoms in the oligomers with $x > 3$ could be reduced. The amount of this fraction can be evaluated from its reoxidation to Cu^{2+}, i.e. from the amount of N_2O detected in NO adsorption measurements (1.3×10^{-4} mol/g from fig. 2a). It corresponds to about 40% of the whole amount of copper present in the zeolite. Moreover, the measurement of O_2 produced during He pretreatment confirms this evaluation (O_2 desorbed $= 6.2 \times 10^{-5}$ mol/g, corresponding to the reduction of 2.5×10^{-4} mol/g of Cu with respect to 6.2×10^{-4} mol/g copper loading, i.e. about 40%).

As an alternative explanation of the obtained results, the possibility that Cu may be exchanged not only at protonic sites associated with framework Al sites, but also at defect sites such as nested silanols at Si vacancy defects [36] must be taken into account. As by increasing the Si/Al ratio the number of such defects can become even higher than the number of Al sites, the average distance of exchanged copper ions decreases allowing Cu self-reduction to occur according to the stoichiometry (2). The effect of Si/Al ratio of Cu-ZSM-5 zeolite on the self-reducibility of copper is under investigation.

5. Conclusions

The transient behaviour of Cu-ZSM-5(640), shown in NO adsorption experiments, gives some useful indication on the redox chemistry of this catalyst. The amount of N_2O produced allowed to quantitatively measure the copper sites that undergo self-reduction in the zeolite. It seems very likely that only Cu sites that are able to move through two possible states of oxidation can be active towards NO decomposition. Moreover, the study of NO adsorption allows one to evaluate that a 40% fraction of this kind of copper is present in the catalyst.

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