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Research Paper

A DFT study on the mechanism of NO decomposition catalyzed by short-distance Cu(I) pairs in Cu-ZSM-5

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ABSTRACT

The complete NO decomposition catalyzed by short-distance Cu^+ pairs in Cu-ZSM-5 was studied by means of DFT calculations. After adsorption of two NO molecules, an hyponitrite species is formed. Further decomposition of hyponitrite occurs with activation energies ranging from about 4 to 24 kcal mol^{-1}, depending on the initial geometry of the substrate-catalyst complex. An oxidized form of the catalyst, $[Cu—O—Cu]^{2+}$ and a copper-coordinating N_2O molecule are obtained. Further N_2O decomposition may occur with oxygen transfer from N_2O to $[Cu—O—Cu]^{2+}$ and formation of N_2 and O_2, both adsorbed on the catalyst. Three different kinds of transition states were identified for the latter step, which appears to be rate-determining due to activation energies ranging from 39–40, to 44–45, and to 50–52 kcal mol^{-1}, respectively. After this, N_2 desorption occurs easily, whereas O_2 desorption is endothermic (from 28.8 to 36.5 kcal mol^{-1}), the highest value being associated to reductive O_2 desorption from a peroxide-like complex. It turned out that the best way for N_2O elimination is the direct, spin-forbidden decomposition on a reduced $Cu^+\cdots Cu^+$ pair, with formation of $[Cu—O—Cu]^{2+}$ and N_2, as already suggested in the literature. The problem of how the reduced catalyst may be regenerated is left open.

1. Introduction

The direct decomposition of NO ($2NO \rightleftarrows N_2 + O_2$) is thermodynamically favoured up to about 1273 K but is rather slow in the gas phase and also in the presence of many catalysts [1–4]. However, since Iwamoto's discovery in 1986 [5,6] it is known that Cu-ZSM-5 is much more active than many other catalysts even at relatively low temperature (673–773 K). Despite the large number of publications on this topic many points are not fully understood, mainly the nature of the active site and the reaction mechanism. It is commonly accepted that the superior activity of Cu-ZSM-5 is related to a small fraction of Cu^{2+} ions, introduced in the ZSM-5 zeolite only at the higher exchange levels [7,8] and easily reduced to Cu^+ under vacuum at 723–773 K [9–11], but there is no agreement about the number of copper ions per active site. Some authors suggested that the reaction occurs on single Cu^+ ions [2,12] but the possibility that active sites may be pairs of Cu^+ ions was also suggested because (i) the turnover frequency (TOF) of the NO decomposition increases with the copper loading, following a peculiar sigmoidal curve with a plateau at about the maximum exchange capacity of the ZSM-5 catalysts [7,8] and (ii) the maximum value of the TOF can be linearly correlated to the number of aluminium atoms per unit cell of the ZSM-5 zeolite [13].

Several computational studies were undertaken on Cu-ZSM-5 and NO decomposition, with the aim to elucidate both the nature of the active site and the reaction mechanism. Some of them were focused on the coordination of copper ions within the ZSM-5 framework and calculated, by means of suitable computational methods [14,15], the binding energy of Cu^+ [16], Cu^{2+} [17], and Cu^+ pairs [18] for different sites and coordination numbers. As far as the reaction mechanism is concerned, it is known from theoretical calculations that the single-step, symmetric, concerted decomposition of two NO molecules is forbidden by orbital symmetry both in the gas phase and on a single Cu^+ site [19]. As a consequence, multi-step mechanisms were proposed for the above reaction on single Cu^+ centres in Cu-ZSM-5 [20–26]. The generally accepted mechanism involves the initial formation of N_2O and of an oxidized ZCuO catalytic centre (Z = zeolite) from two NO molecules. The final products are obtained by decomposition of N_2O, which reacts with ZCuO, leaving N_2 and an O_2 molecule coordinated to ZCu ($ZCu\cdots O_2$) [22–24]. It was also suggested that N_2O may react with a different ZCu site, giving $ZCuO + N_2$. Although the latter reaction is spin-forbidden, a catalytic effect of Cu-ZSM-5 was demonstrated [25,27]. Alternatively, it was suggested that N_2O reacts with a third NO molecule, giving N_2 and NO_2. The latter species reacts with a

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ZCuO unit, leaving NO again and ZCu···O_2. In this way, NO behaves both as the substrate and as an oxygen-carrier, which, through the formation of NO_2, moves an O atom from a catalytic site to another [23,25]. Alternative pathways, involving the formation of the ZCu(NO_2)(NO) and/or ZCu(N_2O_3) intermediates, were found impractical because of the high activation energies required for the decomposition of such species [26].

In a previous work [28] we investigated the mechanism of NO decomposition catalyzed by Cu^+ pairs located at the opposite sides of the ten-membered rings of Cu-ZSM-5 but relatively high activation energies (about 50 kcal mol^{-1}) were calculated for the rate-limiting step of the process, i.e. the reaction of N_2O with the almost linear $[Cu—O—Cu]^{2+}$ fragment, which turned out to be very stable. Liu et al. investigated by DFT calculations the decomposition of N_2O catalyzed by a single Cu^+ site [29] as well as by Cu^+ pairs [30]. In the latter case, activation energies of 47.2 and 63.9 kcal mol^{-1} were respectively calculated when N_2O reacts with the bare $Cu^+···Cu^+$ pair and with the binuclear $[Cu—O—Cu]^{2+}$ species [30]. However, these activation energies turned out to be higher than the corresponding ones calculated by the same authors on a single ZCu or ZCuO site (35.2 and 28.1 kcal mol^{-1}, respectively) [29]. Recently, it was suggested both by experimental and computational work that Cu^+ pairs in Cu-ZSM-5 and other zeolites may be the active site for O_2 activation and consequent CH_4 oxidation to CH_3OH [31–34], as well as for N_2O decomposition [35,36]. The latter reaction, although spin-forbidden, was shown to have a low activation energy (2–15 kcal mol^{-1}) because of the high stability of the binuclear $[Cu—O—Cu]^{2+}$ species formed after release of N_2. According to absorption and Resonance Raman spectroscopy, the active sites should consist of Cu^+ pairs located within the ten-membered rings of the zeolite channels, with the Cu^+ ions coordinated to the lattice oxygens of two Al T-sites separated by two Si T-sites. It was also shown that the most active Cu^+ pairs are those where the Cu—Cu distance is sufficiently short (<4.2 Å) so that N_2O can bind with a bridged μ-1,1-O coordination before reaction [31,35,36].

In the light of the above results, the present work investigates the whole process of NO decomposition catalyzed by Cu^+ pairs located at a short distance, within the so-called M7 ring of the ZSM-5 structure [16,17]. The reason for this choice is that such a potential catalytic site probably represents the lowest limit for the Cu—Cu distance of a Cu^+ pair within the ZSM-5 framework, and therefore the study was aimed at checking whether this may have any special mechanistic implications. In particular, the present research is aimed at evaluating whether a short-distance Cu^+ pair allows N_2O decomposition and N_2/O_2 formation to occur with a lower activation energy with respect to a single-Cu^+ site [20–26,29] and/or to Cu^+ pairs located at a longer distance [28,30], where the above step requires a relatively high activation energy. In general, the limited size of the adopted clusters allows the comparison of a large number of structures optimized at an accurate computational level, starting from NO adsorption, to the formation of N_2O, up to the final release of N_2 and O_2. The main geometrical features of the optimized structures may represent a reasonable starting point for corresponding studies on similar catalytic sites as, for instance, the M6 ring [16,17] of Cu-ZSM-5, or specific sites along the 10-membered rings of the catalyst [31,35,36], where the Cu—Cu distances of the Cu^+ pair are only slightly larger than in the present system and the coordination of Cu^+ to framework oxygen atoms is similar.

2. Methods

The catalytic site, represented by the so-called M7 ring [16,17] of Cu-ZSM-5, was simulated by means of the $Si_7Al_2Cu_2O_{26}H_{16}$ cluster, shown in Fig. 1. In a recent work [37], we showed that the above structure is large enough to account for all the interactions of Cu^+ ions with the zeolite framework as well as for the interactions involved in the adsorption of NO. It was also shown that, at least for the investigated system, the inclusion of a larger portion of the zeolite framework by means of the ONIOM [38–42] approximation does not appreciably change the results with respect to a simple cluster approach [37].

Taking the crystallographic structure of orthorhombic H-ZSM-5 [43] as the starting point, the $Si_7Al_2Cu_2O_{26}H_{16}$ cluster was obtained by Al/Si substitution at the T1 and T7 sites and consequent Cu^+ addition. The free valence of each terminal O atom was saturated by a H atom initially placed 1.0 Å far from the corresponding O, along the bond with the next Si atom not included in the cluster. The total cluster charge was set to zero throughout the calculations, so that a formal Cu^+ ion corresponds to each Al^{3+} ion of the zeolite framework. As in previous work [37,44], geometry optimizations were performed as follows: in a first step, a pre-optimization, all interatomic distances and the Cu^+ coordinates of the $Si_7Al_2Cu_2O_{26}H_{16}$ cluster were optimized keeping the zeolite bond angles and dihedrals frozen at the corresponding crystallographic values. This was done in order both to adapt the system to the Al/Si substitution and to take into account that DFT calculations slightly overestimate Si—O distances with respect to experimental values [14,37,44]. In the second step, all terminal —OH groups of the above cluster were frozen at the positions obtained after the first step in order to maintain the specific geometry constraints of ZSM-5, and the remaining geometrical parameters were fully optimized. The so-obtained cluster was further employed with the same geometrical constraints (frozen —OH groups) to simulate NO adsorption and reactivity. After optimization, each structure was vibrationally characterized, checking for the absence of imaginary frequencies in the minima and for the presence of only one imaginary frequency in the transition states. The great majority of the structures optimized in the present work, unless differently indicated, have a triplet-state wavefunction.

All calculations were performed by the Gaussian-09 code [45] The B3LYP functional [46,47] was employed, both for the sake of comparison with previous work [24–32] and also because less computationally expensive functionals such as, for instance, BLYP [48] or PBE [49,50] were shown to overestimate the adsorption energy of NO [37], thus leading to potential artefacts in the energetics of the investigated reaction paths. The so-called Ahlrichs' "def2" basis sets [51,52] were employed for all calculations as follows: def2-TZV for saturating H atoms, def2-TZVP for N, O, Al, Si and def2-QZVP for Cu. Such a combination of basis sets turned out [44] to minimize the Basis Set Superposition Error (BSSE) both in the coordination of Cu^+ to the zeolite framework and in the interaction of NO with coordinated Cu^+. In particular, BSSE effects in the adsorption energy of NO were shown to be less than 1.0 kcal mol^{-1} [44], which is a rather small value with respect to the energy changes involved in the investigated reaction paths. For this reason, no BSSE corrections are provided in the present work. The output of the calculations was inspected and re-elaborated by the molecular visualization program Molden [53] and figures were obtained by the Mercury [54] software.

3. Results and discussion

In the crystal structure of ZSM-5 [43], the so-called M7-rings [16,17,37,44] are found in specular pairs on the walls of the linear channels, which run along the *b* crystal axis (Fig. 1). Each pair of specular rings is delimited by a pair of parallel sinusoidal channels (which run along the *a* crystal axis) so that the M7-rings are also at the intersection between the linear and the sinusoidal channels. T1 sites are exactly at the edge between the linear and the sinu-