Journal of Catalysis 366 (2018) 189–201

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

The mechanism of NO and N_2O decomposition catalyzed by short-distance Cu(I) pairs in Cu-ZSM-5: A DFT study on the possible role of NO and NO_2 in the $[Cu—O—Cu]^{2+}$ active site reduction

Simone Morpurgo

Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", P.le Aldo Moro 5, 00185 Roma, Italy

ARTICLE INFO

Article history:
Received 12 June 2018
Revised 6 August 2018
Accepted 7 August 2018

Keywords:
Cu-ZSM-5
NO decomposition
N_2O decomposition
DFT
Computational
Kinetics
Energetic span model

ABSTRACT

The reactivity between NO and the oxidized form of a short-distance dinuclear Cu-ZSM-5 catalyst (ZCu_2O) was investigated. ZCu_2O, which contains the $[Cu—O—Cu]^{2+}$ bridge coordinated at the opposite T11 positions of the M6 ring of ZSM-5, is obtained by the spin-forbidden decomposition of N_2O on the reduced form of the catalyst, ZCu_2, with an activation energy of about 18 kcal mol^{-1}. The further addition of NO to the $[Cu—O—Cu]^{2+}$ unit of ZCu_2O occurs in the doublet state without activation energy and gives NO_2. After desorption, which requires 39.9 kcal mol^{-1}, NO_2 decomposes on a second ZCu_2O site, giving NO again and O_2. Three reaction paths were defined for the latter reaction, with activation energies ranging from about 30 to 42–43 kcal mol^{-1}. Final O_2 desorption is endothermic. The effect of enthalpy and Gibbs free energy contributions at 298.15 and at 773 K was also shown and discussed. According to the present calculations, the $[Cu—O—Cu]^{2+}$ bridge can easily be broken by reaction with NO but the desorption and further decomposition of NO_2 are characterized by energetics which make the above mechanism slower than the spin-allowed decomposition of N_2O on similar sites, already reported in the literature. The above conclusions were based on a kinetic analysis according to the Energetic Span Model.

1. Introduction

Since Iwamoto's discovery in 1986 [1,2] it is known that at relatively low temperature (673–773 K) Cu-ZSM-5 is a very effective catalyst for the direct decomposition of NO ($2NO \rightleftarrows N_2 + O_2$) otherwise slow in the gas phase and in the presence of many other catalysts [3–6]. However, after more than thirty years since the original publications and despite the large number of studies on this topic, the nature of the active site and the corresponding reaction mechanism are not yet fully understood. Some authors initially suggested that the reaction occurs on single Cu^+ ions [4,7–9] but the hypothesis that active sites may be pairs of Cu^+ ions was also formulated on the basis of several experimental observations [10–16] mainly related to the dependence of the turnover frequency (TOF) on the number of aluminium and copper ions per unit cell of the catalyst.

Several computational studies were undertaken with the aim to understand the reasons of the special activity of Cu-ZSM-5 for NO decomposition. The coordination of copper ions to the zeolite framework was investigated by specifically conceived computational methods [17,18] calculating the binding energy of Cu^+ [19], Cu^{2+} [20], and Cu^+ pairs [21] within different potential catalytic sites and assuming variable coordination numbers. As far as the reaction mechanism is concerned, theoretical calculations also showed that the single-step, symmetric and concerted decomposition of two NO molecules is forbidden by orbital symmetry both in the gas phase and on a single Cu^+ site [22]. As a consequence, multi-step mechanisms were proposed for the above reaction on single Cu^+ centres in Cu-ZSM-5 [23–31]. 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 ($ZCu\cdots O_2$) [25–27]. 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 [28–30]. 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 ZCuO unit, leaving NO again and $ZCu\cdots O_2$. In this way, NO behaves both as the substrate and as

---

E-mail address: simone.morpurgo@uniroma1.it

https://doi.org/10.1016/j.jcat.2018.08.006
0021-9517/© 2018 Published by Elsevier Inc.

an oxygen-carrier, which, through the formation of NO_2, moves an O atom from a catalytic site to another [26,28]. 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 [31].

In a previous work [32] we investigated by DFT calculations 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. Even higher values (63.9 kcal mol^{-1}) were calculated by other authors [33] for the same reaction step but on a different dinuclear Cu^+ site, suggesting that activation energies may be strongly dependent on the distance between copper ions within a Cu^+ pair.

Experimental and computational studies also suggested that Cu^+ pairs in Cu-ZSM-5 and other zeolites may be the active site for O_2 activation and related CH_4 oxidation to CH_3OH [34–37], as well as for N_2O decomposition [38,39]. The latter spin-forbidden reaction was shown to have a rather low activation energy (2–15 kcal mol^{-1}) on Cu-ZSM-5 because of the high stability of the dinuclear $[Cu—O—Cu]^{2+}$ species formed after release of N_2. It was also shown that, among different Cu^+ pairs, the most active are those where the $Cu\cdots Cu$ distance is sufficiently short (<4.2 Å) so that N_2O can bind with a bridged μ-1,1-O coordination before reaction [34,38,39].

In a recent work [40] we investigated a possible complete mechanism of NO decomposition, catalyzed by short-distance (~4 Å) Cu^+ pairs in Cu-ZSM-5. In particular, we calculated an activation energy of 38–40 kcal mol^{-1} for the spin-allowed $N_2O + [Cu—O—Cu]^{2+} \rightarrow [Cu\cdots Cu]^{2+} + N_2 + O_2$ reaction, and of about 15 kcal mol^{-1} for the spin-forbidden $N_2O + [Cu\cdots Cu]^{2+} \rightarrow [Cu—O—Cu]^{2+} + N_2$ reaction. In the latter case, the activation energy of N_2O decomposition is rather low but the related mechanistic problem is represented by the need to re-obtain the reduced $[Cu\cdots Cu]^{2+}$ pair in order to restart the catalytic cycle. In this perspective, experimental studies suggested an important role played in the mechanism by NO itself and by NO_2, the first species behaving not only as the substrate but also as a promoter for N_2O decomposition [13,14], and the second one being a possible reaction intermediate [15,16]. In the above studies it was hypothesized that NO may react with an oxidized form of the catalyst to give NO_2, but a detailed description of the possible mechanism was not given, especially for the final NO_2 decomposition. Moreover, it was reported that the presence of NO in the reaction medium has different effects, positive for the reaction catalyzed by single-Cu^+ sites, slightly negative when Cu^+ pairs are involved [13,14]. The aim of the present study is therefore to investigate by DFT calculations the possible reaction of NO with the $[Cu—O—Cu]^{2+}$ unit of oxidized Cu-ZSM-5, which results in NO_2 formation, and the subsequent NO_2 decomposition on a similar catalytic site. Detailed energetics are shown and discussed. The energetic profiles obtained from theoretical calculations are quantitatively analysed by means of the *Energetic Span Model*, developed by Kozuch and Shaik [41–46], which allows to calculate and compare the Turnover Frequencies (TOFs) of reaction mechanisms.

2. Methods

The catalytic site, represented by the so-called M6 ring [19,20,47] of Cu-ZSM-5, was simulated by means of the $Si_{40}Al_2Cu_2O_{109}H_{50}$ cluster, shown in Fig. 1. Taking the crystallographic structure of orthorhombic H-ZSM-5 [48] as the starting point, the above cluster was obtained by Al/Si substitution at the T11 and T11′ tetrahedral 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. In the present work, a larger cluster was adopted with respect to previous studies [32,40] in order to take into account the possible effects of the zeolite framework when calculating potential energy curves for the substrate approaching the active site up to final coordination, but not only at a strict contact with the active site. Having considered the relatively large cluster size, a two-layer ONIOM [49–53] approximation was adopted. The outer part of the cluster was treated at the B3LYP/LANL2DZ level, which was already shown [54] to reproduce the geometry of Cu-ZSM-5 with acceptable results. The adoption of a quantum mechanical approach for the outer region of the ONIOM cluster appeared to be preferable, in principle, to that of Molecular Mechanics (MM) because the parametrization of MM force fields is generally based on specific geometries and

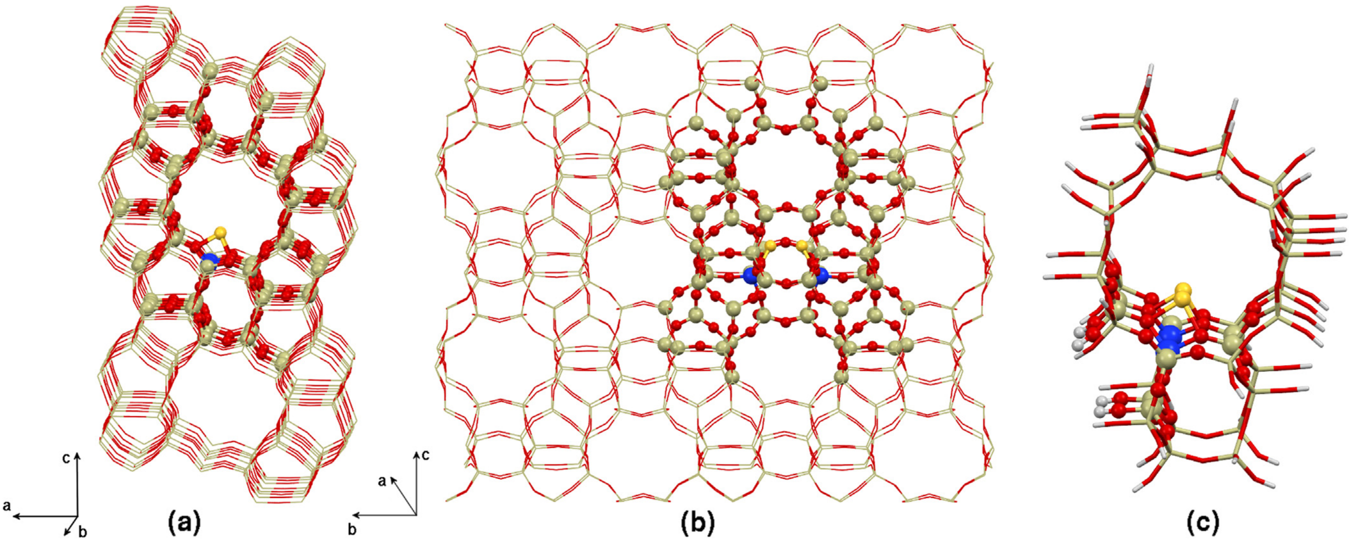

Fig. 1. Location of the investigated cluster within the crystal structure of ZSM-5 viewed along (a) the linear channels and (b) the sinusoidal channels; (c) the $Si_{40}Al_2Cu_2O_{109}H_{50}$ cluster employed in the calculations. The high-level region within the ONIOM approximation is represented as ball-and-sticks, the low-level one as only sticks.