Quantum chemical study of nitrous oxide adsorption and decomposition on Lewis acid sites

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Density functional calculations demonstrate that ordinary Lewis sites containing three- and five-coordinated Al are unlikely to decompose N_2O, since the formation of a weak Al–O bond does not compensate the N–O bond rupture. The ground state of the calculated cluster–oxygen adsorption complexes is triplet. The considered hypothetical site $Al(OH)_4AlO$ can be reactive towards the N_2O decomposition with the heat -17.8 kcal/mol and activation barrier 19.7 kcal/mol.

Keywords: nitrous oxide decomposition, zeolites, Lewis sites, density functional calculations, triplet oxygen stabilization

1. Introduction

During the last decade, the use of N_2O as an oxidant in hydrocarbon selective oxidation reactions has drawn much attention. Excellent reviews on this subject were presented recently in [1–3]. Although a number of transition metal oxides, especially vanadium and molybdenum oxides [4], reveal noticeable activity, nowadays, zeolites are more promising, particularly those of MFI type [5]. As far as the mechanism of the hydrocarbon selective oxidation with N_2O is concerned, there are various opinions [1]. Nevertheless, it is widely accepted that it is the N_2O activation on the reaction center which is the first step of the reaction. For the case of transition metal oxides it is natural to assume that the reaction center consists of a metal ion with a vacancy in its coordination sphere. The structure of the reaction center in zeolites is more questionable and, traditionally, scientists focus first on Brønsted and Lewis acid sites. Some authors propose that N_2O is activated on zeolite acid sites [6–8]. At the same time, there exists an alternative point of view that zeolite activity in catalytic decomposition of N_2O is associated with transition metal impurities present in the zeolite, particularly iron, and which are very difficult to avoid during synthesis [9]. This suggestion was supported in recent experimental studies [10]. It was shown that in the presence of iron in a ZSM-5 sample nitrogen appears after N_2O deposition already at 150 °C, whereas molecular oxygen is evolved only at 350 °C. In contrast, when a ZSM-5 sample lacks iron, nitrogen and oxygen evaluate simultaneously at 500 °C. A similar pattern was observed for a pure Al_2O_3 surface [11]. Thus, the N_2O activation character on an Fe-containing sample is rather different from that on the sample lacking iron.

Quantum chemical studies of N_2O decomposition on extra-framework iron oxide–hydroxide clusters, which are likely to be formed in zeolites, reveal their high activity [12,13]. Another possible type of active sites, which was considered in [14], may be formed from small Fe oxide or hydroxide moieties in zeolite cationic positions. For both the types it was concluded that two structures containing the active oxygen may appear after N_2O decomposition, namely, an oxo and a bridging peroxo species, the transition between them being possible [14]. A similar conclusion was made about analogous structures found in a theoretical study of the methane monooxygenase active site [15].

In the context of the further discussion of the alternative pathways of nitrous oxide activation on zeolites, it is interesting to carry out quantum chemical calculations of the decomposition of N_2O on zeolite acid sites. Previously, in the work by Zholobenko et al. [16] a calculation of N_2O adsorption on a Lewis site, which was modeled by three-coordinated Al^{3+}, was carried out. Qualitative comparison of the calculated data with the results of infrared studies led the authors [16] to the conclusion that such a site may be reactive in nitrous oxide decomposition.

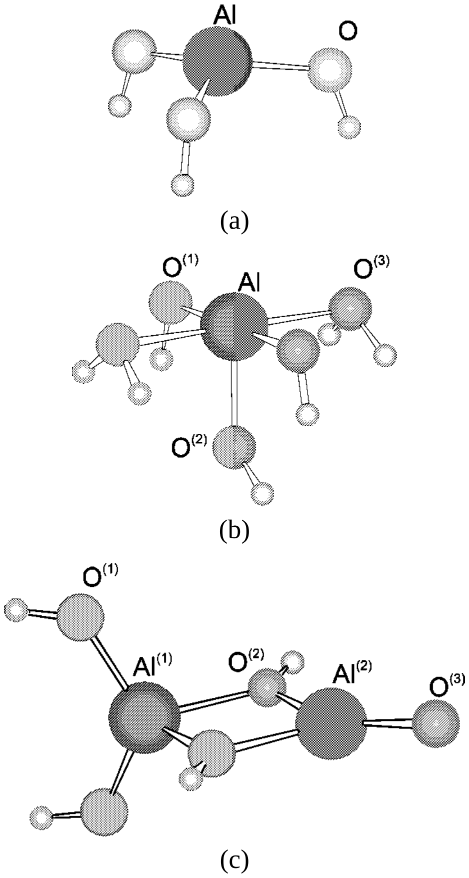
A very interesting question is that about the role of Brønsted acid sites (BAS) in the catalytic oxidation of hydrocarbons by N_2O [17–19]. In the literature, there are opposite points of view on this subject. In [17,18], it was suggested that Brønsted sites participate in hydrocarbon oxidation, whereas in [19] it was demonstrated that catalyst's activity in the benzene to phenol oxidation decreases with BAS concentration.

In this work we present the results of density functional calculations of adsorption complexes of N_2O with different Lewis sites and of products of the catalytic nitrous oxide decomposition on them. Lewis sites were simulated by widely accepted cluster models: three- and five-coordinated Al^{3+} ions [20,21]. As a possible alternative to them, a cluster model of a “non-traditional” Lewis site, the AlO^+ moiety in a zeolite cationic position, was also considered. A gallium analogue of this site was suggested in [22].

2. Computation details

For density functional calculations the quantum chemical package GAUSSIAN92/DFT [23] was employed. The Becke3–Perdew86 exchange–correlation potential [24,25] was used throughout. The standard Pople 6-31G* basis sets were used for all elements.

For the models of Lewis sites we have chosen $Al(OH)_3$ (C_{3v} point group), $Al(OH)_3(H_2O)_2$ (C_{2v}) and $Al(OH)_4AlO$ (C_{2v}) clusters, previously used in quantum chemical studies of CO adsorption on γ-Al_2O_3 and in zeolites [20,21]. Although such models of Lewis sites are small, they are still widely used in quantum chemical calculations (see, for example, [26]). In order to take account of spatial constraints imposed by the crystal lattice on the structure of the adsorption site, one has to restrict some internal coordinates of the molecular model. For example, a four-coordinated Al^{3+} ion ideally has near-tetrahedral geometry of its surrounding, whereas for a three-coordinated one a planar structure is most stable. The two geometries correspond to angles between main order symmetry axis and an equatorial Al–O bond of 109.5 and 90°, respectively (figure 1). To take account of the effect of the surrounding we kept the angle in the $Al(OH)_3$ model frozen at 100°. In [21] this approach was proved to be reasonable. For the model of the Lewis site with five-coordinated aluminum the above mentioned angle was kept fixed at 90°. Further discussion of these models can be found elsewhere [20,21]. The models of ordinary Lewis sites $Al(OH)_3$ and $Al(OH)_3(H_2O)_2$ are further referenced to as X, when discussed together. The $Al(OH)_4AlO$ cluster model can be considered as an AlO^+ moiety in a zeolite cationic position.



(a)

(b)

(c)

Figure 1. Cluster models of the Lewis sites: (a) $Al(OH)_3$, (b) $Al(OH)_3(H_2O)_2$ and (c) $Al(OH)_4AlO$.

In the $Al(OH)_3$ and $Al(OH)_3(H_2O)_2$ clusters all internal variables were optimized within the corresponding symmetry group, except for the angles discussed above. In the $AlO(OH)_3$ and $AlO(OH)_3(H_2O)_2$ clusters the adsorbed oxygen atom was placed along the main symmetry axis. After that, the same internal coordinates plus the Al–O_{ads} distance were optimized. The geometry of the $Al(OH)_4AlO$ cluster and its derivatives were fully optimized within the C_{2v} point group. In the present work, the heat of N_2O adsorption and stabilization energy of atomic oxygen, which is the dissociation product of the former, for the described cluster models were computed. The latter was calculated as the heat of the reaction: $X + O_{(triplet)} \rightarrow XO$. The BSSE corrections were calculated but they appeared to be insignificant (<1 kcal/mol) because of the weak substrate–adsorbate binding.

3. Results and discussion

The cluster models of Lewis sites under discussion are presented in figure 1. Geometry optimization results, as well as adsorption and desorption energies, are summarized in tables 1 and 2. The calculations showed that N_2O is weakly adsorbed on the Lewis sites. The same trend as for carbon monoxide adsorption [14,21] was observed: the adsorption energy on the three-coordinated aluminum site is higher than that on the five-coordinated one. This is no surprise because the former is known to be a stronger Lewis site and has a higher affinity to nucleophilic molecules.

Stabilization energies of the oxygen atom on cluster models of ordinary Lewis sites (table 2) are obviously insufficient to compensate the N–O bond rupture. According to our DFT calculations, the N–O bond dissociation energy is 54 kcal/mol when the resulting oxygen atom is in

Table 1
Calculated geometry parameters of cluster models of Lewis sites. Angles are in degrees, distances in Å.

Cluster	R(Al–O)	∠(O–Al–Z)
$Al(OH)_3$	1.71	100
$Al(OH)_3(H_2O)_2$		
$R(Al–O^{(1)})$	1.78	90
$R(Al–O^{(2)})$	1.85	180
$R(Al–O^{(3)})$	2.04	90
$Al(OH)_4AlO$		
$R(Al^{(1)}–O^{(1)})$	1.70	118
$R(Al^{(1)}–O^{(2)})$	1.85	39
$R(Al^{(2)}–O^{(2)})$	1.82	140
$R(Al^{(2)}–O^{(3)})$	1.60	0

Table 2

DF calculated properties of cluster models of Lewis sites in the N_2O decomposition reaction: energies of N_2O adsorption, $E_{\mathrm{ads}}(N_2O)$, N_2 desorption, $E_{\mathrm{des}}(N_2)$, and atomic oxygen stabilisation, $E_{\mathrm{st}}(O_{\mathrm{ads}})$, in kcal/mol, as well as Al–O_{ads} distances, in Å, before and after nitrogen desorption.

Substrate cluster	$E_{\mathrm{ads}}(N_2O)$	R(Al–N_2O)	$E_{\mathrm{des}}(N_2)$	$E_{\mathrm{st}}(O_{\mathrm{ads}})$	R(Al–O_{ads})
$Al(OH)_3$	−19.9	2.02	45.5	−28.7	1.89
$Al(OH)_3(H_2O)_2$	−10.8	2.12	42.0	−22.6	1.92
$Al(OH)_4AlO$	−5.3	2.20	−17.8	−77.4	1.72

triplet state, and 121 kcal/mol when it is singlet. Therefore, the N_2O dissociation on these clusters is endothermic. A similar result was obtained in an earlier theoretical study [12] of another model of a three-coordinated Al^{3+} site formed upon partial dehydroxylation of a binuclear fragment of aluminum hydroxide $(OH)_2Al(OH)_2Al(OH)_2$. Those calculations were carried out employing the semiempirical NDDO/MC method. Our results are also in agreement with experimental findings [27] that no correlation exists between Lewis sites concentration and the catalyst's activity in the benzene partial oxidation reaction.

It is noteworthy that ground states of the XO (where $X = Al(OH)_3$ or $Al(OH)_3(H_2O)_2$) clusters are triplet and their lowest singlet states lie higher by 39 and 44 kcal/mol, respectively. Since the adsorption complexes of N_2O with substrate clusters all have closed shell, there must be a prohibitive singlet–triplet transition on the reaction course. The electronic structure of the XO clusters is another argument against the stabilization of the atomic oxygen on the Lewis sites. The HOMO–LUMO gap in the clusters is as little as 1.1–1.2 eV. Besides that, the spin density in the ground state of the clusters is primarily located on the adsorbed oxygen atom, $q_a(O_{\mathrm{ads}}) = 1.67$ a.u. in $AlO(OH)_3$ and $q_a(O_{\mathrm{ads}}) = 1.63$ a.u. in $AlO(OH)_3(H_2O)_2$, indicating that it has substantially atomic character and is very weakly stabilized by the substrate clusters.

To make sure that the results are stable with respect to the method employed, we repeated calculations for the model of the three-coordinated Al^{3+} Lewis site using the MP2 method. According to the MP2 calculation, the triplet oxygen atom is stabilized by 21 kcal/mol, while the cluster's singlet state energy is higher by 29 kcal/mol. The Al–O_{ads} distance in singlet state is 2.08 Å whereas in triplet it is 1.78 Å, close to the DFT result. Thus MP2 results are consistent to DFT ones. Unlike the MP2 case, geometry optimization of the $AlO(OH)_3$ cluster in the triplet state at the Hartree–Fock level results in R(Al–O_{ads}) = 2.1 Å. Moreover, spin density distribution in the $AlO(OH)_3$ cluster in the HF case is such that 100% of it is located on the adsorbed oxygen atom. Thus, taking the electronic correlation into account mitigates the well-pronounced unperturbed character of the adsorbed oxygen atom, but does not change the conclusions. Interestingly, the triplet oxygen has been recently identified experimentally in the CH_3Cl matrix at 11 K, existing in the form $CH_3Cl\cdots O$ [28].

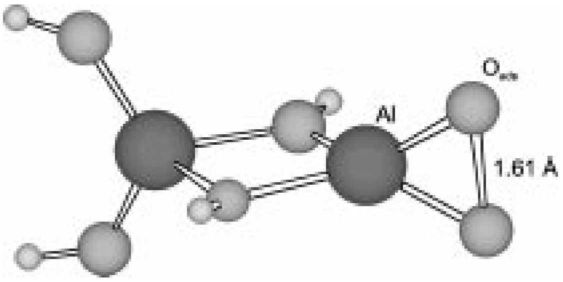
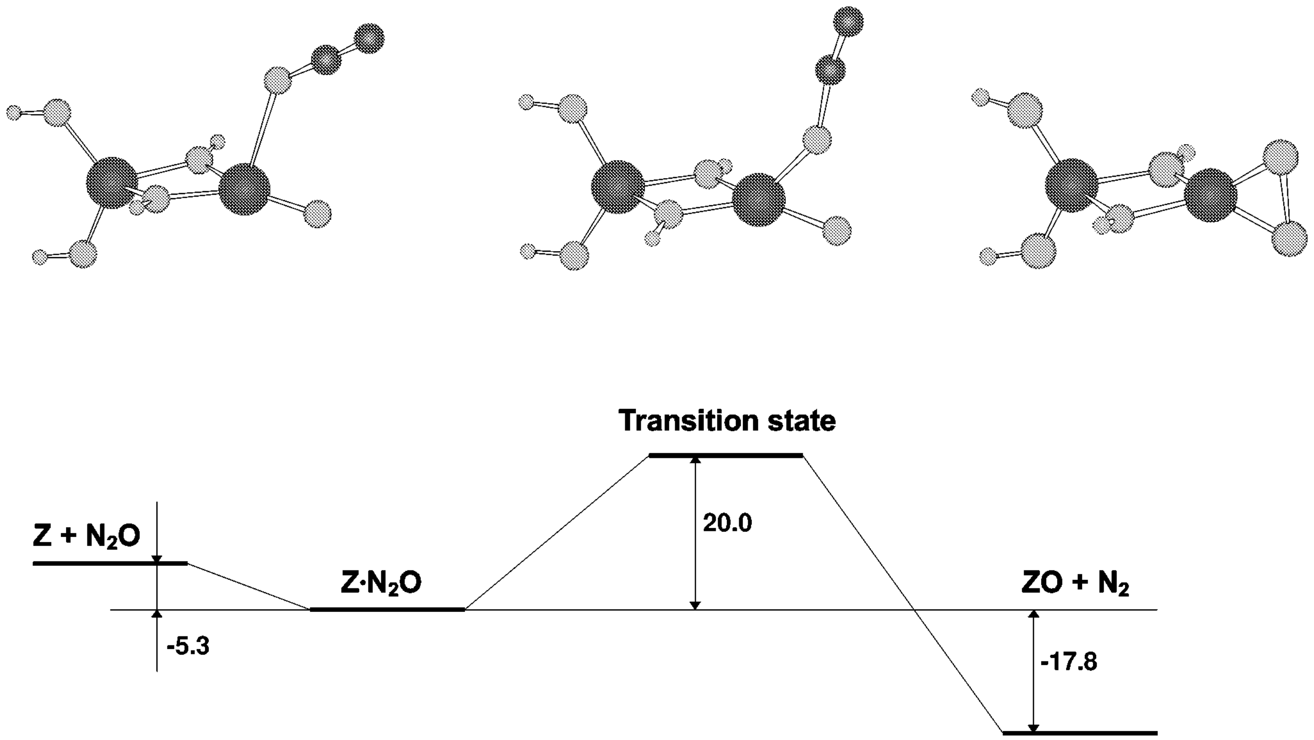


Figure 2. The structure of the $Al(OH)_4AlO_2$ cluster formed after N_2 desorption from the $Al(OH)_4AlO\cdot N_2O$ adduct.

For the $Al(OH)_4AlO$ cluster model completely different results were obtained. The heat of N_2O molecular adsorption on the cluster is lower than that on both the ordinary Lewis sites (table 2). However, upon N_2 desorption a quasi-peroxide structure $Al(OH)_4AlO_2$ (figure 2) is obtained, with R(O–O) = 1.61 Å, indicating that there is a weak oxygen–oxygen bonding. This results in the oxygen stabilization energy as large as 77.4 kcal/mol, yielding the total energy effect of −17.8 kcal/mol. The resulting cluster has closed electronic configuration, thus the nitrogen desorption is not spin-prohibited. Recently, a structure similar to the $Al(OH)_4AlO_2$ cluster, namely AlO_2AlO_2, was considered in [29] as one of the isomers of the Al_2O_4 molecule. There, a singlet and triplet state structures were calculated employing the B3LYP density functional, the latter being lower that the former by 34.4 kcal/mol. Interestingly, the terminal O–O distance in the singlet state was calculated to 1.66 Å, close to our 1.61 Å.

Taking this in account, it seems natural to estimate the reaction barrier of the N_2O dissociation on the $Al(OH)_4AlO$ cluster, therefore we carried out a calculation of the reaction transition state. The calculation results are presented in scheme 1. The activation barrier of 20 kcal/mol makes it possible to decompose nitrous oxide of the site, provided that it exists. Although the existence of this type of sites was suggested in [22] with regard to their gallium analogue, the presence of such reactive sites in zeolites is questionable and requires experimental support. In particular, the results of theoretical calculations of the IR spectrum of adsorbed CO on such a center [20,21] may be used as a starting point for experimental search. It was shown that this type of sites should be very reactive towards alkanes [22,30], but it is unlikely to be regenerated in the catalytic cycle [31].



Scheme 1. Results of the calculation of the reaction path of N_2O decomposition on the $Al(OH)_4AlO$ cluster (denoted as Z). Energies are given in kcal/mol.

4. Conclusions

The DFT calculations of N_2O interaction with Lewis sites showed that N_2O dissociation on ordinary models of Lewis sites containing three- and five-coordinated Al^{3+} is endothermic, since the energy gain due to the Al–O bond formation is not sufficient to compensate the N–O bond rupture. Ground states of the resulting XO ($X = Al(OH)_3$, $Al(OH)_3(H_2O)_2$) clusters are triplet (in contrast with the singlet state of $X{\cdot}N_2O$ complexes), which implies an inhibiting singlet–triplet transition upon N_2O desorption. Calculations predict that nitrous oxide decomposition on the hypothetical $Al(OH)_4AlO$ site takes place with an energy gain -17.8 kcal/mol, given that such sites exist. A calculation of the reaction path of N_2O dissociation on the $Al(OH)_4AlO$ cluster results in a 20 kcal/mol activation barrier.

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