Catalysis Letters 40 (1996) 17–23

Selective oxidation of methane by dinitrogen monoxide on FeZSM-5 zeolites. Ab initio quantum chemical analysis

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Received 22 January 1996; accepted 29 March 1996

On the basis of ab initio quantum chemical calculations, we propose the structure and energetics of the species taking part in the selective oxidation of methane by dinitrogen monoxide on FeZSM-5 zeolites. The immediate oxidizing site is reasonably represented by a binuclear iron-hydroxide cluster with a peroxo-like fragment located between iron atoms.

Keywords: FeZSM-5 zeolites; selective oxidation of methane; dinitrogen monoxide; α-oxygen; binuclear iron-hydroxide clusters; peroxo fragment; Hartree–Fock and MP2 calculations

1. Introduction

The possibility to produce oxygen-containing organic compounds via direct partial oxidation of saturated hydrocarbons, is very attractive to be used in oil and petrochemical industries. However, being rather inert, alkanes are usually activated under hard conditions resulting in low reaction selectivity.

On the other hand, zeolites are well known to be excellent activators of saturated hydrocarbons [1]. Recently, a very interesting class of catalytic reactions over FeZSM-5 zeolites was discovered [2–7]. The latter show unusual activity in the selective oxidation of various compounds (alkanes, benzene, carbon monoxide) by dinitrogen monoxide. Such reactions involve adsorption and decomposition of N_2O which, at temperatures below 300°C, results in selective formation of the reactive form of surface oxygen (called α-oxygen) [7]:

$$N_2O + Z \rightarrow N_2O \cdots Z \tag{1}$$

$$N_2O \cdots Z \rightarrow N_2 + OZ \tag{2}$$

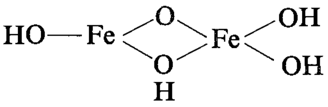
where "Z" denotes the corresponding active site on the FeZSM-5 zeolite surface, and "OZ" the superactive oxidizing center.

A thus prepared zeolite sample is then treated with the compound to be oxidized. In particular, methane is converted to methanol with an almost 100% yield. Oxidation occurs very rapidly at room temperature resulting in the formation of a complex of methanol with the FeZSM-5 surface,

$$CH_4 + OZ \rightarrow CH_3OH \cdots Z \tag{3}$$

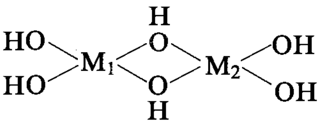
with subsequent extraction of methanol by acetonitrile and water [8].

Due to the absence of any direct structural information on the FeZSM-5 samples (e.g., X-ray diffraction data), simulating the structure of active sites met serious difficulties. However, numerous calorimetric [4], infrared [6], mass-spectrometric and ESR [7], and Mössbauer spectroscopy data [9] on the species involved in processes (1)–(3) are available. These data provide valuable information to construct a model of the active site in FeZSM-5 zeolites. The first model of the Z center was suggested in ref. [10] in the form of the lowest-spin binuclear cluster with stoichiometry $Fe_2O_3 \cdot 2H_2O$ (product of partial dehydration of iron(III)-hydroxide dimer),



whose formation may occur as iron escapes from the ZSM-5 lattice during thermal treatment of the samples. There are several arguments in favor of this model.

Above all, iron(III) is well known to show structural similarity with aluminum in oxygen-containing compounds [11]. Therefore, some useful information can be obtained by analogy with corresponding aluminum-containing structures. For instance, the formation of Lewis acid centers is one of the most extensively discussed problems that attracted attention to the process of dealumination in zeolites. It has been shown [12,13] that the initial stage of dealumination is likely to involve binuclear bridged clusters,



where M_1, M_2 = Al (i.e., dimers of aluminum hydroxide). Therefore, the cluster with one or two aluminum atoms substituted by iron can be considered as a possible precursor in forming the Z center. The structures with $M_1 = M_2 = Al$; $M_1 = Al$, $M_2 = Fe$; and $M_1 = M_2 = Fe$ have been analyzed in ref. [10] on the basis of quantum chemical calculations using the semiempirical NDDO/MC method [14]. It has been shown [10] that only the last variant (i.e., with two iron atoms) can be regarded as a reasonable source to form the Z center. Let us consider some indirect experimental evidence of the binuclear nature of the species under study.

Firstly, the stoichiometric ratio of α-oxygen to iron measured for different FeZSM-5 samples never exceeds 1 : 2 [9].

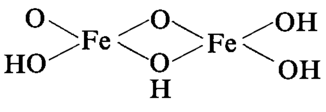
Secondly, the catalytically active state of iron in FeZSM-5 is invisible for ESR, which is consistent with the formation of binuclear complexes with iron atoms coupled antiferromagnetically (α-oxygen in the OZ site is not detected by ESR spectroscopy as well) [7].

Thirdly, according to the Mössbauer spectroscopy data on the species under study, the parameters of iron atoms lie in the region typical for oxo-bridged binuclear iron complexes ([9] and references therein).

Finally, a deep similarity was observed between process (3) and the enzymatic oxidation of methane to methanol in the presence of methane monooxygenase [9]. On the other hand, the active center of the latter is known to include two iron atoms [15]. Therefore, one could expect the active site in FeZSM-5 zeolites to be a binuclear cluster as well.

One should note that the clusters under consideration are not of model character only. There is a wide variety of well-characterized oxo- and hydroxo-bridged diiron complexes with an antiferromagnetic coupling between iron atoms [16].

Based on the structure of the Z center discussed above, the authors of ref. [10] have proposed the structure of $N_2O\cdots Z$ and OZ clusters and estimated the heats of reactions (1) and (2). According to ref. [10], the α-oxygen of the OZ center is involved in a ferryl fragment ($Fe^{IV}O$),



The results of ref. [10] may be regarded as a first successful attempt to construct the model of the active site in FeZSM-5 zeolites. However, to satisfy the modern requirements to theoretical models of real systems and processes, one should check semiempirical results with those of high-level quantum chemical calculations (ab initio Hartree–Fock and post-Hartree–Fock, density functional theory, etc.). Thus, in this paper we would like to analyze the reasonability of the models of Z and OZ centers [10] on the basis of ab initio quantum chemical calculations as well as to study the ways of oxidizing cleavage of methane on the OZ center (3).

2. Computational details

All the clusters under study were considered at their lowest-spin (singlet) states on the reasons discussed above (our estimates of the energy of triplets showed them to be significantly higher than that of singlets).

Full geometry optimization of the clusters (Berny optimization method [17]) has been performed at the closed-shell Hartree–Fock level of theory (HF) using the LANL1DZ basis set (Los Alamos effective core potential [18] and valence double-zeta for Fe, and D95V valence double-zeta basis set for other atoms [19]). No symmetry constraints were imposed on the geometrical parameters of the structures except for the Z center itself which is considered to be within the C_s symmetry group. This level of theory (HF/LANL1DZ) is employed below when discussing the geometrical and electronic structure of the clusters (section 3.1).

To take into account electron correlation effects, we have performed single-point MP2 calculations (second-order Møller–Plesset perturbation theory) using an all-electron polarized double-zeta basis set supplemented by polarization (diffuse) functions for all non-hydrogen atoms (denoted as DZP). For iron atoms, the latter consists of a basis set [20] supplemented with one diffuse d-function and recontracted in its d-part according to ref. [21] ((14s9p6d) primitive Gaussians are contracted to [8s4p3d] by using the (62111111/4212/411) scheme). For oxygen, nitrogen and carbon atoms, we have used a (9s5p)/[4s2p] basis set [22] ((6111/41) contraction scheme) supplemented with a polarization d-function according to ref. [23] (exponents 0.92, 0.93 and 0.78, respectively); and for hydrogen atoms, the basis set from ref. [24] (contraction (41)) has been employed. Thus, the heats of reactions as well as the relative stabilities of the clusters are considered at the MP2/DZP//HF/LANL1DZ level of theory (section 3.2).

We did not treat the basis set superposition error (BSSE), since reactions (1)–(3) are accompanied by an appreciable structural rearrangement, and, hence, may not be considered as simple addition–elimination processes (see figs. 1–5). Therefore, using the counterpoise method [25] would be quite ambiguous since there is no justified and unique way to locate ghost orbitals.

All the computations have been performed using the GAUSSIAN 92/DFT software package [26], on the Sun SPARCstation 10 MP.

3. Results and discussion

3.1. Geometrical and electronic structure of the Z center and related clusters

To obtain the optimized geometry of the Z center and its adduct with N_2O, we started from the corresponding structures obtained in ref. [10] in the frame-

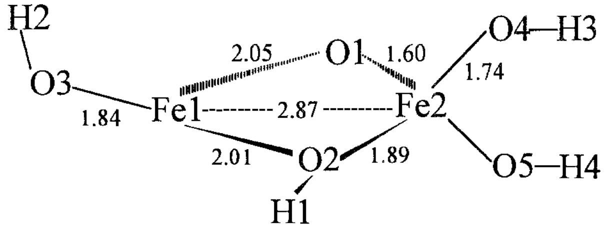


Fig. 1. Geometrical structure of the Z center in FeZSM-5 zeolites. Interatomic distances are in angstroms.

work of the NDDO/MC method [14]. According to our ab initio calculations, the equilibrium geometry of the Z center (fig. 1) is qualitatively similar to that of ref. [10] (structure II therein) with some differences in the values of bond lengths and bond angles due to the difference in the quantum chemical methods employed.

Fig. 2 presents the structure of the $N_2O\cdots Z$ adduct. As in the case of the Z center itself, a topological similarity with the corresponding NDDO/MC one (structure III of ref. [10]) is observed. Namely, the N_2O molecule is attached via its oxygen end to the three-coordinated iron of the Z center (Fe1). It should be pointed out that our ab initio calculations give a value of the Fe1–O6–N1 angle equal to 126° unlike the collinear disposition of corresponding iron, oxygen and nitrogen atoms in ref. [10]. The angle of 126° seems to be more reasonable because of the sp^2-hybridized character of the oxygen atom in the N_2O molecule (its lone electron pairs should form an angle of about 120° with the O–N bond). On the other hand, there is the experimental justification of the "declined" disposition of the N_2O molecule in the related species. Such a way of N_2O coordination with an aluminum atom in the mixed Al–Fe Lewis acid site was proposed in ref. [27] on the basis of ^{15}N NMR data on dinitrogen monoxide adsorbed on H-ZSM-5 zeolites.

Now let us consider the possible structures of the OZ center. As mentioned above (section 1), NDDO/MC calculations predict for α-oxygen to be a lone oxygen atom linked with one iron atom and thus involved in a ferryl fragment, $Fe^{IV}O$ (structure V of ref. [10]). However, our ab initio studies of the topologically similar structure have shown for the latter to correspond to neither a local minimum nor a transition state. Taking the structures similar to V of ref. [10] as initial guesses (with various combinations of bond lengths and angles), we have obtained a cluster with rather distinguished geometry after the geometry optimization procedure had been completed. The result (cluster OZ1) is presented in fig. 3.

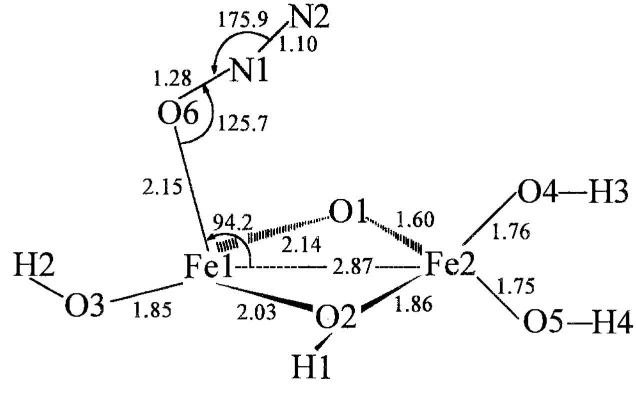


Fig. 2. Geometrical structure of the complex of N_2O with the Z center on the FeZSM-5 surface ($N_2O\cdots Z$). Interatomic distances are in angstroms, angles are in degrees.

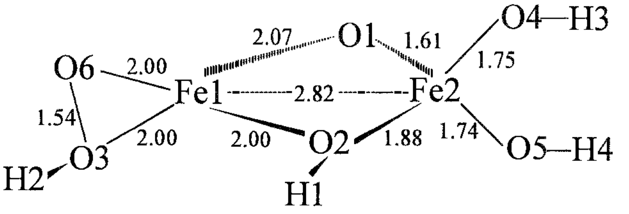


Fig. 3. Geometrical structure of the cluster OZ1 representing the inactive form of surface oxygen. Interatomic distances are in angstroms.

One can see that the "extra" oxygen atom in the OZ1 cluster, O6, is involved in the fragment with shortened O–O distance (1.54 Å). The latter is close to the O–O distance in hydrogen peroxide (1.44 Å). Thus one may say about the well-pronounced peroxide fragment, O3–O6 in OZ1 species. Such peroxo complexes of transition metals are extensively discussed in literature [28].

The electronic structure of the OZ1 cluster is rather complicated as a whole. However, since we are interested in the oxidizing ability of OZ1, it would be sufficient to restrict ourselves to considering its lowest unoccupied molecular orbital (LUMO) only. Our analysis shows the latter to have a very low eigenvalue (−0.07 eV) as expected for a strong oxidizer. The LUMO mainly consists of Fe2 d-orbitals and has admixtures of orbitals centered on the neighboring oxygen atoms. Since the formation of the transition state in the course of the oxidation process should obviously involve the LUMO of the oxidizer, one can expect the "immediate oxidizing site" to be localized near the Fe2 atom. On the other hand, there is no appropriate source of oxygen in the vicinity of Fe2 of cluster OZ1. One can see from fig. 3 that the peroxo fragment O3–O6 is separated from Fe2 by more than 4 Å (being linked with the Fe1 atom only). Thus,

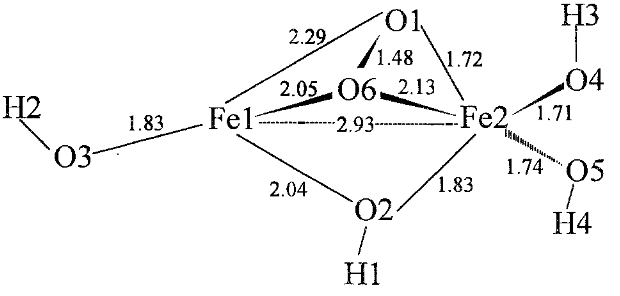


Fig. 4. Geometrical structure of the cluster OZ2 representing the active form of surface oxygen (α-oxygen). Interatomic distances are in angstroms.

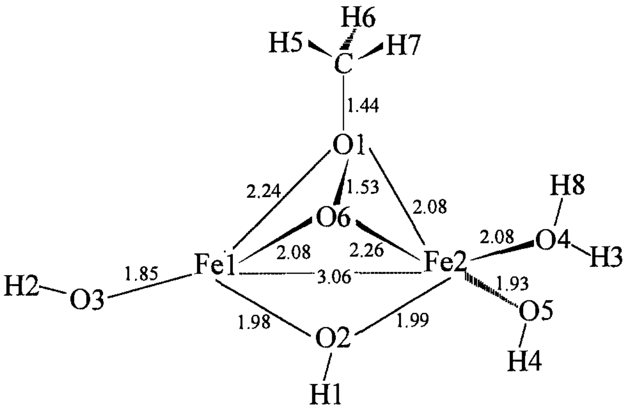


Fig. 5. Geometrical structure of the complex of methanol with the Z center in FeZSM-5 zeolite ($CH_3OH\cdots Z$) that is formed as a result of methane oxidation on the OZ2 site. Interatomic distances are in angstroms.

OZ1 seems to be inactive in the reaction of methane oxidation (3).

The formation of an OZ1 cluster may be considered as a result of moving extra oxygen O6 outside the four-membered iron–oxygen ring after dinitrogen has been eliminated from the $N_2O\cdots Z$ adduct. Therefore, searching for an alternative structure of the OZ site may start from the natural supposition that the O6 can also move toward an Fe2 atom. In this case, one could expect the formation of a peroxo-like fragment anywhere in the space between both iron atoms that would provide the suitable source of oxygen to be involved into oxidation of methane.

Our ab initio calculations have shown that such a structure does really exist. Fig. 4 presents the geometrical structure of the stable cluster (OZ2) with extra oxygen involved in the Fe1–O6–O1–Fe2 fragment. It should be noted that the quantum chemical simulation of water photooxidation in the presence of iron-containing catalysts [29] has shown that some intermediates contain such Fe–O–O–Fe fragments.

One can see from fig. 4 that Fe1–O6 and Fe2–O6 distances are very close to each other (2.05 and 2.13 Å, respectively). As for the Fe1–O1 to Fe2–O1 ratio (see below), the latter is similar for all the clusters considered (figs. 1–4). Thus, OZ2 can be also regarded as a tri-bridged cluster. A similar structure was proposed in ref. [15] as a probable active center for methane monooxygenase.

Characteristics of the LUMO of OZ2 are qualitatively similar to those of OZ1 (low eigenvalue, −0.79 eV, and predominant contribution due to Fe2 d-orbitals). Thus, our choice of OZ2 cluster as a model of immediate active site for the methane oxidation seems to be reasonable.

The next problem was associated with the possible ways of oxidizing cleavage of methane and with the structure of the $CH_3OH\cdots Z$ adduct. It was clear that at least one of the "peroxide" oxygens (O1 or O6) should be involved in the oxidation. A priori we expected participation of both atoms. However, our ab initio simulations have shown that the O6 atom plays only an auxiliary role in breaking the C–H bond (probably, O6 participates in the formation of the transition state). The stable structure of $CH_3OH\cdots Z$ is formed according to the following way of methane cleavage: CH_3 goes to O1, and H to O4 (fig. 5).

Unfortunately, we failed in finding the intermediate structure of reaction (3). As we mentioned above, in practice this process occurs almost instantaneously at room temperature, and no retardation of the reaction was observed up to −50°C [8]. Therefore, its activation barrier should be very small (experimental estimations give the value of about 1.2 kcal/mol [9]). Available methods for transition state search [17,30] are probably too rough to locate a so low-lying saddle point.

Before considering the energetics, we would like to discuss possible ways of assigning oxidation states to iron atoms in the binuclear clusters under study. Though oxidation states do not follow immediately from quantum chemical calculations, some conclusions can be deduced from the structural peculiarities of the clusters and from the qualitative comparison of the Mulliken charges on iron atoms. A priori, one could propose a Fe^{III}–Fe^{III} scheme for Z and $N_2O\cdots Z$ clusters, since the Z cluster is naturally considered as a product of partial dehydration of an iron(III)-hydroxide dimer (see section 1). However, there are some arguments in favor of the alternative scheme, Fe^{II}–Fe^{IV}.

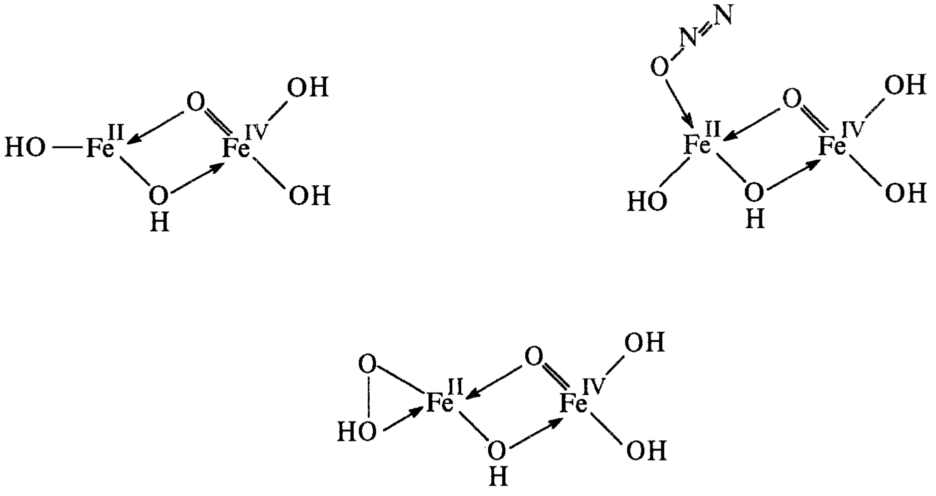
Firstly, our ab initio calculations showed that the positive charges of Fe1 in Z, $N_2O\cdots Z$ and OZ1 clusters (1.29, 1.30 and 1.31, respectively) are appreciably lower than those of Fe2 (1.44, 1.43 and 1.45).

Secondly, one can see from figs. 1–3 that the Fe2–O1 distance in Z, $N_2O\cdots Z$ and OZ1 clusters is significantly shorter than the Fe1–O1 distance (by approximately 0.5 Å). Such a short metal–oxygen distance (about 1.6 Å) may indicate the presence of a double bond (e.g., in vanadyl ion, VO^{2+}, V–O distance is 1.56 to 1.59 Å [31]). Therefore, one can regard the Fe2 atom to be involved in a ferryl fragment ($Fe^{IV}{=}O$) in the clusters under study. Thus, the schematic representation of scheme 1 seems to be valid (arrows denote donor–acceptor interaction).

Such a representation can be used to explain why the OZ structure with "dangling" oxygen [9] is instable in our calculations: the Z cluster already has one ferryl group, and the formation of another $Fe^{IV}{=}O$ fragment (associated with α-oxygen) is hardly possible.

3.2. *Energetic aspect of processes involving the Z center and related clusters*

Table 1 lists the total energies of clusters (see figs. 1–5), and those of the small molecules involved in the reactions under study. One can see from table 1 that the energy of the OZ2 cluster is lower by 0.0723 au



Scheme 1.

(45.4 kcal/mol) than that of OZ1. Thus, the formation of the tribridged structure OZ2 responsible for the oxidation of methane is more preferable that that of the inactive OZ1 site. However, these data do not allow us to conclude that only OZ2 can arise as a result of the thermal decomposition of FeZSM-5/N_2O samples. To show this, it is enough to compare the calculated heats of the reactions with available thermochemical data [4,32] (table 2).

Let us consider the summary reactions (4a) and (4b) ((1) + (2a) and (1) + (2b), respectively). Here we use the calorimetric data [4] on N_2O decomposition on FeZSM-5 zeolites with oxygen fixation obtained at different temperatures within the range of 200–275°C. Within experimental error, the heats measured [4] do not depend on the temperature, but do depend on surface oxygen loading, θ. Namely, the absolute value of ΔH_0^0 decreases (from 24.5 to 19.5 kcal/mol) with increasing θ.

On the other hand, according to ref. [33], not all surface oxygen, but only a certain portion is active in methane oxidation (the portion depends on the conditions of FeZSM-5 sample preparation and of surface oxygen loading). Such an unusual effect can be explained by the existence of at least two different forms of surface oxygen as a result of thermal decomposition of adsorbed N_2O. As one can see from table 2, the heats [4] lie within the range between the calculated heat of formation of OZ1 and that of OZ2. Thus, one may conclude that both OZ1 and OZ2 species (inactive and active form of the surface oxygen, respectively) are formed.

Attention should be paid to the heats of dioxygen elimination from OZ1 and OZ2 clusters ((5a) and (5b) of table 2). The experimental heats [4] have been obtained indirectly from (4a), (4b) and (6). Obviously, they fall into the range between the calculated values since the real process is simply a superposition of reactions (5a) and (5b) within the model proposed. The low experimental binding energy of surface oxygen was used in ref. [4] as a justification of the high activity of oxygen loaded FeZSM-5 in the oxidation of methane. However, our calculations show that just the active form of surface oxygen (OZ2) is characterized by a rather high energy of oxygen elimination (in contrast to OZ1 whose decomposition (5a) is an exothermic process like that of usual peroxo compounds). Thus, in our opinion, considering the oxidation process as a simple insertion of the weakly bonded oxygen atom into the C–H bond of methane needs some revision.

As to the heat of reaction (3), our calculations predict the latter to be almost zero (table 2). Unfortunately, there are no corresponding experimental data for comparison. However, our result seems to be reasonable if we take into account the similarity observed between FeZSM-5 zeolites and methane monooxygenase with respect to the methane oxidation [9]. Enzymatic reactions are known to proceed under very soft thermal con-

Table 1

Total energies of clusters (figs. 1–5) and corresponding small molecules, at the MP2/DZP//HF/LANL1DZ level of theory [a]

Cluster	Total energy (au)	Molecule	Total energy (au)
Z	−2902.35788	N_2	−109.26275
$N_2O\cdots Z$	−3086.66112	N_2O	−184.21824
OZ1	−2977.33250	$O_2, s = 1$ [b]	−149.98069
OZ2	−2977.40483	CH_4	−40.31462
$CH_3OH\cdots Z$	−3017.71893	CH_3OH	−115.22015

[a] See section 2 for details concerning basis sets.

[b] The ground $^3\Sigma_g^-$ state for dioxygen molecule was calculated using the UHF and UMP2 approximation.

Table 2
Heats of reactions calculated as sum of ab initio (MP2/DZP//HF/LANL1DZ) total energies of products [$\sum E_t$(prod)] minus that of reagents [$\sum E_t$(reag)] [a]. Available experimental data are included. Numbering of the reactions corresponds to that of section 1

	Reaction	Calculated $\sum E_t$(prod) - $\sum E_t$(reag) (kcal/mol)	Experimental ΔH_0^0 (kcal/mol)
(1)	$N_2O + Z \rightarrow N_2O\cdots Z$	−53.3	
(2a)	$N_2O\cdots Z \rightarrow N_2 + OZ1$	+41.3	
(2b)	$N_2O\cdots Z \rightarrow N_2 + OZ2$	−4.1	
(3)	$CH_4 + OZ2 \rightarrow CH_3OH\cdots Z$	+0.3	
(4a)	$N_2O + Z \rightarrow N_2 + OZ1$	−12.0	−24.5 to −19.5 (±3.5) [b,c]
(4b)	$N_2O + Z \rightarrow N_2 + OZ2$	−57.4	
(5a)	$OZ1 \rightarrow Z + \frac{1}{2}O_2$	−9.9	+6.0 to +1.0 (±3.5) [b,c]
(5b)	$OZ2 \rightarrow Z + \frac{1}{2}O_2$	+35.5	
(6)	$N_2O \rightarrow N_2 + \frac{1}{2}O_2$	−21.9	−20.4 [d] −18.5 (±0.5) [b]

[a] See section 2 for details concerning basis sets.
[b] Data from ref. [4].
[c] Species OZ1 and OZ2 are indistinguishable in calorimetric measurements.
[d] Data from ref. [32].

ditions. The thermal effect of such reactions should not be high at each stage, otherwise a destruction of the enzyme may occur [34]. Thus, in our opinion, the isoenergetic character of reaction (3) can be considered as an additional indirect argument in favor of the results [9] regarding FeZSM-5 as a man-made model of methane monooxygenase.

4. Conclusions

Based on ab initio quantum chemical calculations, we have proposed the structure and energetics of the species taking part in the selective oxidation of methane by dinitrogen monoxide on FeZSM-5 zeolites. The initial active site (Z center) is reasonably simulated by a binuclear asymmetric bridged iron-hydroxide cluster that readily forms an adduct with dinitrogen monoxide ($N_2O\cdots Z$). Decomposition of $N_2O\cdots Z$ yields at least two forms of surface oxygen represented by OZ1 and OZ2 clusters. The former contains a peroxo fragment linked with one iron atom only, whereas the latter includes a peroxo-like fragment located between both iron atoms. Only OZ2 shows activity with respect to the oxidation of methane and easily splits the latter with the formation of the surface complex $CH_3OH\cdots Z$. The oxidation itself proceeds with almost zero thermal effect.

Acknowledgement

This research was made possible in part by Grant No. RBH300 from International Science Foundation and Russian Government. We are grateful for intensive discussions to Professor G.I. Panov, Drs. V.I. Sobolev, K.A. Dubkov and A.S. Kharitonov. AVA is thankful also to Dr. V.I. Avdeev for his help in carrying out the calculations.

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