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On the ferryl catalyst: Electronic structure and optimized *ab initio* geometry

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ABSTRACT

Full geometry optimizations have been carried out in order to determine the structure of the global minimum for the quintet state of the isolated α-center $[FeO]^{2+}$ using the neutral cluster $OFe(OH)_2$ as a model. The intrinsic reaction coordinate and a potential energy cut were calculated aiming at the examination of other low-energy structures. The absolute minimum here reported for the title species differs from the structures reported in other molecular orbital-based studies. Such a structure has been analyzed in order to determine the oxidation state of the Fe atom in the ferryl catalyst.

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1. Introduction

The Fe/ZSM-5 catalyst became a subject of interest due to the selective oxidation of hydrocarbons by N_2O [1,2]; an example is the highly selective (around 95%) oxidation of benzene to phenol [2]. The catalytic activity is related to the Fe^{2+} species [3]. An oxidative center, $[FeO]^{2+}$, is formed during the decomposition of N_2O on the active sites [3–5] of the Fe/HZSM-5 system:

$$N_2O + Fe^{2+} \rightarrow [FeO]^{2+} + N_2$$

The α-oxygen species so formed are very reactive in oxidation reactions [2,4,5] but tend to be stable in the absence of reagents. This α-oxygen center, $[FeO]^{2+}$, is bonded to the zeolite through O or OH groups. It can be described using the valence bond schemes $Fe^{IV} = O$ and $Fe^{III} - O\cdot^{-}$[closecurl]; however, these are different states of the α-oxygen center rather than resonance structures, and hence it is unknown which of them is found under catalytic conditions [2,6–9]. Many studies [5,10–13] have been performed aiming at the determination of the oxidative state of the Fe atoms. Despite the evidence provided by resonant inelastic X-ray spectroscopy [14] of the presence of $Fe^{III} - O^{-}\cdot$ in the α-oxygen center, there is no certainty concerning the state that compels an oxidative reaction. For this reason, it is very important to determine the electronic structure of the $[FeO]^{2+}$ system.

A large number of studies has been performed using density functional theory [10,15,16]; however, the results obtained with this single-determinant approach are in many cases not reliable, especially for 3*d* transition metal compounds (see the review by Cramer and Truhlar [17], and the analysis of this problem by Kaplan [18,19]). Note that even the simplest 3*d*-electron systems, dimers, can only be precisely calculated by the multireference configuration interaction method [20,21] (indeed, we should emphasize that single-reference MO methods face severe problems in describing 3*d*-systems).

The oxidation state of Fe in an α-center has been suggested from experimental work to be $+2$ [22,23]. Assuming that ferrous iron in zeolites is qualitatively equivalent to free iron coordinating two OH groups (which usually withdraw almost two electrons from the iron atom), Zilberberg et al. [6] carried out calculations to study the electronic structure of atomic oxygen adsorbed in the ferrous α-center Fe(II)–O using $OFe(OH)_2$ as a neutral model of $[FeO]^{2+}$. They have performed complete-active-space self-consistent-field (CASSCF [24]) calculations using (10e,9o) as the active space, which consists of the 3*d* and 4*s* orbitals of Fe and the 2*p* orbitals of O. The dynamical correlation was further obtained by the multiconfigurational quasi-degenerate perturbation theory (MCQDPT) [25,26] as well as DFT/B3LYP [27,28] calculations. CASSCF optimized geometries of all states have been reported, as well as constrained CASSCF potential energy scans, with the ground state of $OFe(OH)_2$ being predicted [6] to be $^5A_1$. Analogous scans were obtained using MCQDPT corrections using CASSCF optimized geometry for various states. The above authors [6] have further given an analysis of the occupancies of the natural orbitals for all the states and presented the main electron configuration for the bonding. They concluded that there are three covalent bonds of the σ and π types involving the oxygen and ferrous iron. In addition, potential energy curves were reported [6] for all states, with the $^5A_1$ state shown to dissociate to $O^- + Fe(OH)^{2+}$ based on the occupancies of the natural orbitals. Upon such an analysis, it was concluded that the electron

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configuration in the dissociation limit corresponds to $Fe^{3+} + O^-$. Optimized geometries were also given [6] for the various states (triplets, quintets, and septets).

All structures presented in Ref. [6] are planar and symmetrical with respect to the H atoms; see structure (a) in Figure 1. The C_{2v} symmetry has been assumed [6,8] in all calculations, thus implying the equivalence of the two bridged oxo centers which bind the iron center to the zeolite lattice.

In order to obtain optimized geometries with multi-reference perturbation theory calculations, Malykhin et al. [8] published a further study using the same $OFe(OH)_2$ model: they applied the fully optimized reaction space (FORS) variant of CASSCF theory [29] and the intruder-state-avoidance multireference perturbation theory (ISA-MRPT) [30] method. The active space, (10*e*,10*o*), included the five 3*d* orbitals of the iron atom, three 2*p* orbitals of oxygen and two diffuse-like orbitals. The authors [8] carried out geometry optimizations for triplet, quintet and septet states with ISA-MRPT. They reported the same ground state, $^5A_1$ and compared the results obtained for this state with the other low-lying one $^5B_2$. The optimized geometry for the ground state is structure (a) in Figure 1; it is the same geometry as reported in Ref. [6]. However, Malykhin et al. [8] proposed yet another structure, Figure 1b, to analyze the influence of the geometry on the electronic structure of the active species.

The authors [8] anticipated that the ground state should be $^5A_1$ at the employed CASSCF and ISA-MRPT levels of theory if structure (b) of Figure 1 were used instead of (a). The same C_{2v} symmetry restriction has been used [8].

It should be mentioned that for transition metal compounds the CASPT2 method can predict an artificial stability [31]; this approach and even the more sophisticated multireference *n*-electron valence state perturbation theory (NEVPT) [32] approach do not give a reliable Mulliken population, see discussion in Ref. [21].

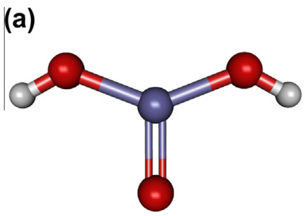
In this Letter, we report the results obtained for the above $OFe(OH)_2$ neutral model of the isolated α-center $[FeO]^{2+}$ using the CASSCF and multireference configuration interaction (MRCI) methods. It is worthwhile noting that the real geometry of the α-center is still unknown, since in all published calculations the crystal field of zeolite was not taken into account.

2. Methodology

We have used here the same molecular model, namely $OFe(OH)_2$. The methods employed were CASSCF [33,34] and MRCI [35,36] with the Dunning-type cc-pV*X*Z ($X = 3, 4$) basis set of Balabanov and Peterson [37] and smaller basis sets: 6–31G** for Fe [38], 6–31G* for O [39] and 6–311G** for H [39], named hereinafter 6–31G* for the sake of brevity. The active space (10*e*,9*o*) is defined by the 4*s* and 3*d* orbitals of Fe and the 2*p* orbitals of O. Full geometry optimizations (all 12 parameters were taken into account) have been performed without symmetry restrictions for the lowest energy structure and transition state of the quintet molecular term; the intrinsic reaction coordinate (IRC) calculations were also performed. Both the geometry optimizations and IRC calculations were done using the quadratic steepest descent (QSD) optimization method of Sun and Ruedenberg [40] at both CASSCF/6–31G* and CASSCF/cc-pV*X*Z levels of theory. The CASDC (an abbreviation of CASSCF and dynamical correlation) scheme proposed by Varandas [41], which follows from the partition $E_{MRCI} = E_{CAS}(r) + E_{dc}(r)$ of the molecular energy, was followed for the IRC calculations. This is based on a four point premise [41,42]:

1. Bond-breaking/bond-forming reactions are best treated by multireference methods such as MRCI, preferably when the Davidson correction Q [43,44] is added, MRCI + Q.
2. A convenient reference for MRCI is the full-valence-complete-active-space (FVCAS) wave function, warranting in principle a correct description at dissociation.
3. Can be described by a single reactive coordinate.
4. Single-point MRCI + Q calculations along the optimized FVCAS path should differ marginally from the unaffordable directly optimized MRCI + Q ones.

The results obtained in smaller systems [41,42] are accurate, and hence we also expect reliable results from the present calculations which are not too computationally demanding, an attribute that might be extreme for the system here studied. Nevertheless, the minimum was optimized at both MRCI/6–31G* and MRCI/cc-pVTZ levels of theory. The convergence criteria used for the optimizations and the IRC calculations were 10^{-6} for the gradient and 10^{-8} for the energy in all CASSCF calculations; for the MRCI optimizations of the minimum, the convergence criteria were 10^{-4} for the gradient and 10^{-6} for the energy. The harmonic vibrational frequencies were also calculated. The MRCI energies are corrected by means of the Davidson scheme [43,44], in order to approximately correct for quadruple electronic excitations and diminish size-inconsistency. All calculations were carried out with the MOLPRO [45,46] suite of programs.



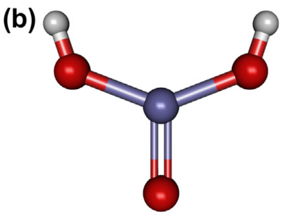


Figure 1. The conformations of $OFe(OH)_2$ obtained in Refs. [6,8]. The central atom of the structures is Fe (dark gray color), oxygen atoms are in red color and H atoms in white. Structure (a) is the geometry reported in both studies as the ground state. Structure (b) was proposed in Ref. [8] as another model to study the influence on geometry on the electronic structure.

3. Results

3.1. Geometry optimization

We have calculated the optimized geometries of both the minimum and transition states. For the former, the structures obtained are planar irrespectively of basis set, except for the structure of the transition state, where one of H atoms is out of the plane; the values of the involved dihedral angles are $\theta_3 = 247.68$, 261.99 and 258.53°, with the 6–31G*, cc-pVTZ and cc-pVQZ basis sets, respectively. The transition state structure was optimized only at the CASSCF level of theory. In Table 1 all optimized parameters obtained with the CASSCF method and various basis sets are presented, while Figure 2 shows the structures obtained. In all the presented plots, the central atom is Fe; as usual, O atoms are in red, H atoms in white.

The minimum has also been MRCI optimized with the 6–31G* and cc-pVTZ basis. The bond distance Fe–O in the α-oxygen center is shorter at the MRCI level than at the CASSCF one. All other bond distances remain essentially unaltered in both methods. The angles are slightly modified but the structures remain planar. The parameters obtained from the MRCI optimization of the minimum are presented in Table 2.

Harmonic frequencies and total energies for both the minimum and transition states are presented in Table 3. The optimized geometry of the minimum is planar and not symmetric with respect to the OH bonds, in contrast to the structures presented

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