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Formation of an Iron-Oxo Species upon Decomposition of Dinitrogen Oxide on a Model of Fe-ZSM-5 Zeolite

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The so-called "α-oxygen" on Fe-ZSM-5 zeolite, a surface oxygen species responsible for high reactivity in oxidation of methane and of benzene, has been investigated. We present from density-functional-theory (DFT) calculations how such a reactive surface species is generated upon decomposition of dinitrogen oxide (N_2O) and propose a possible form of "α-oxygen" on Fe-ZSM-5 zeolite. In the initial stages of the reactions, a complex involving an $Fe(ON_2)$ moiety is formed, followed by dissociation into an iron-oxo species and N_2. The activation energy for the decomposition of N_2O on a possible iron active site model of Fe-ZSM-5 zeolite is predicted to be 2.4 kcal mol^{-1} at the B3LYP level of theory. Therefore the decomposition of N_2O is expected to take place easily at a coordinatively unsaturated iron active center supported on zeolite. The iron-oxo species thus formed should play an essential role in the direct hydroxylation of methane, benzene, and other hydrocarbons if it involves a coordinatively unsaturated iron. The oxygen exchange on the iron-oxo complex was also investigated. The activation energy for the oxygen exchange on the "α-oxygen" is predicted to be 26.8 kcal mol^{-1}. We propose that the bare FeO^+ complex and the so-called "α-oxygen" on Fe-ZSM-5 zeolite involve similar catalytic active centers responsible for similar catalytic functions for methane and benzene.

The direct conversions of methane to methanol[1] and of benzene to phenol[2] have attracted the attention of researchers in pure and applied chemistry for many years. Such a direct process for the hydroxylation of benzene was discovered in 1982 by Iwamoto et al.,[3] as a gas-phase process indicated in reaction (1). Phenol was formed from benzene in the presence of water over various transition-metal oxides supported on silica gel using dinitrogen oxide (N_2O) as an oxidizing reagent. The best result was obtained by using vanadium oxide supported on silica gel; the selectivity for phenol attained approximately 70% at 10% conversion levels of benzene on 3.3 wt% V_2O_5/SiO_2 at 823 K. $O^{\bullet -}$ radical generated from N_2O decomposition was proposed to play a role in this interesting reaction.[3]

$$C_6H_6 + N_2O \rightarrow C_6H_5OH + N_2 \qquad (1)$$

ZSM-5 zeolite proved to show a high catalytic selectivity for the oxidation of benzene to phenol.[4—6] A surface oxygen species generated on Fe-ZSM-5 zeolite under N_2O-decomposition conditions has been proposed to be responsible for the high reactivity of the catalytic system; such an oxygen species was called "α-oxygen" by Panov et al.[7] Accordingly, we use the term "α-oxygen" for the active surface species of Fe-ZSM-5 zeolite throughout this paper. According to Ref. 8d, to increase the concentration of α-centers of Fe-ZSM-5 zeolite, air calcination should be followed by activation in vacuum at 900 °C for 1 h, and finally by treatment with O_2 at 550 °C. Two modes of decomposition of N_2O over ZSM-5 zeolite were observed: At 200 °C the reactive oxygen species associated with iron impurities is formed, and at 450 °C molecular oxygen is formed. In reaction (2), ( ) means "α-center" of Fe-ZSM-5 zeolite.[7] The unknown oxygen species generated at 200 °C, indicated by (O) in reaction (2), was suggested to play an essential role in the benzene hydroxylation over Fe-ZSM-5 zeolite, as indicated in reaction (3). The conversion of methane to methanol is also catalyzed over Fe-ZSM-5 zeolite at room temperature; "α-oxygen" is also proposed to be responsible for the catalytic reactivity toward methane, as in reaction (4).[8]

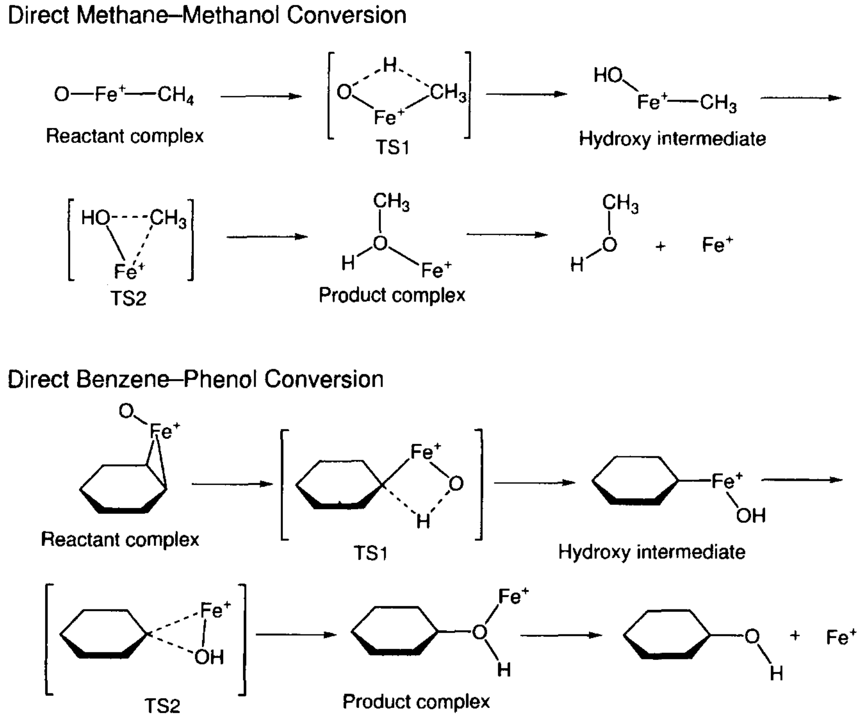
$$N_2O + (\ ) \rightarrow (O) + N_2 \qquad (2)$$

$$(O) + C_6H_6 \rightarrow C_6H_5OH \qquad (3)$$

$$(O) + CH_4 \rightarrow CH_3OH \qquad (4)$$

Several features of "α-oxygen" are described in Ref. 7: (1) "α-oxygen" is formed on Fe-ZSM-5 zeolite but not on other iron-containing catalysts; (2) It is loosely bound to the surface of Fe-ZSM-5 zeolite; (3) It is thermally stable up to 300 °C; (4) It is produced upon N_2O decomposition but not upon O_2 adsorption; (5) It exhibits high reactivity in oxidation of methane, benzene, and carbon monoxide as well as in oxygen isotopic exchange.

There are interesting gas-phase reactions that are closely related to the zeolite-catalyzed oxidation reactions mentioned above. Schröder and Schwarz[9—11] showed that the bare FeO^+ complex reacts with methane and benzene under ion cyclo-



Scheme 1.

tron resonance (ICR) conditions, giving methanol and phenol, respectively, in high yields. The direct oxygen-atom transfers from the transition-metal oxide are of great interest because these processes can be viewed as a model of catalytic and enzymatic hydrocarbon hydroxylation. Thus, a detailed analysis of these gas-phase reactions is the key to understanding the catalytic hydrocarbon hydroxylation over Fe-ZSM-5 zeolite and to developing a high-performance catalytic system. In previous papers,[12] we have demonstrated that the direct hydroxylation of methane by the FeO^+ complex should take place in a two-step concerted manner, as shown in Scheme 1; moreover, we recently proposed that the same mechanism is applicable to understand the electronic processes of the direct benzene hydroxylation by FeO^+.[13] We have successfully applied this concerted mechanism to the methane hydroxylation[14] by intermediate **Q** of soluble methane monooxygenase (sMMO), in which a dinuclear iron complex plays an essential role as an active site.[15]

The reactive FeO^+ complex is formed in the gas phase from the reaction of Fe^+ with pulsed-in N_2O; when Fe^+ is generated in the presence of N_2O, first-order decay of the Fe^+ signal is observed with a corresponding increase of the FeO^+ signal.[16] As mentioned earlier in this paper, "α-oxygen" is also formed upon decomposition of N_2O over Fe-ZSM-5 zeolite.[7] Thus, there are interesting features common to the catalytic reactions over Fe-ZSM-5 zeolite and the gas-phase reactions using the bare FeO^+ complex. Taking cognizance of the previous studies mentioned above, we set up a working hypothesis that "α-oxygen" should have relevance to a surface species involving an iron-oxo species as an active catalytic center. We reasonably assume that the gas-phase reactions by the FeO^+ complex and the catalytic reactions over Fe-ZSM-5 zeolite should take place in similar fashions. This is quite reasonable if a coordinatively unsaturated (less than six-coordinate) iron-oxo species is responsible for the C–H bond activation of methane and benzene.

It is therefore important to investigate how such a reactive iron-oxo species is generated upon decomposition of N_2O because of possible implications for the rational design of high-performance catalysts. Recently, Stirling[17] computed and analyzed the dissociation of N_2O by the first-row transition metals (Sc, Ti, and V), concerning the ground-state, spin-conserving reactions. From semiempirical quantum-chemical calculations using dinuclear model complexes, Filatov et al.[18] proposed that N_2O decomposition does not occur at an Al atomic center but does occur at an Fe atomic center. This result may give a hint as to the still unknown structure of "α-oxygen" on Fe-ZSM-5 zeolite. The subject of this paper is to elucidate a possible correlation between the bare FeO^+ complex and "α-oxygen" on Fe-ZSM-5 zeolite. We present from density-functional-theory (DFT) calculations the mechanism and the energetics for the formation of the reactive iron-oxo species from dinitrogen oxide and propose a possible form of reactive "α-oxygen" on Fe-ZSM-5 zeolite.

Method of Calculation

We used the hybrid density-functional-theory (DFT) B3LYP method,[19,20] implemented with the Gaussian 94 ab initio program.[21] This method consists of the Slater exchange, the Hartree–Fock exchange, the exchange functional of Becke,[19] the correlation functional of Lee, Yang, and Parr (LYP),[20] and the correlation functional of Vosco, Wilk, and Nusair.[22] The contribution of each energy to the B3LYP energy expression was fitted by Becke[19] empirically on a reference set of molecules. This hybrid DFT method has been reported to provide excellent descriptions of various reaction profiles, particularly in geometries, heats of reaction, barrier heights, and molecular vibrations.[23] For the Fe atom we used the (14s9p5d) primitive set of Wachters,[24] and for the H, N, O, Al, and Si atoms we used the 6-31G** basis set,[25] a standard double-zeta basis set with polarization function. Vibrational frequencies were systematically computed for all stationary points obtained in order to confirm that each optimized geometry corresponds to a local minimum that has no imaginary frequency or to a saddle point that has only one imaginary frequency. Zero-point-energy corrections were taken into account in calculating the energetics of reaction pathways.

Results and Discussion

Formation of the FeO^+ Species from Dinitrogen Oxide. The active species toward methane and benzene, i.e., the bare FeO^+ complex in the gas-phase reactions and "α-oxygen" on ZSM-5 zeolite, are generated from the decomposition of N_2O. In order to better understand the direct methane–methanol and benzene–phenol conversions, we first consider how the bare FeO^+ complex is generated in the gas phase. Computed B3LYP energy diagrams for the formation of the FeO^+ complex in the sextet and the quartet spin states are shown in Fig. 1. The sextet potential energy surface plays a dominant role in this decomposition reaction, and accordingly this is essentially a spin-conserving reaction. We thus pay our attention to the sextet potential energy diagram. Optimized structures for the initial complex and the transition state of the sextet state are also indicated in the illustration. In the early stages of the reaction, Fe^+ and N_2O come into contact to form the $Fe^+(ON_2)$ complex, the computed binding energy being 10.4 kcal mol^{-1} in the sextet state. The "end-on" $Fe^+(ON_2)$ complex is then dissociated into FeO^+ and N_2 via a transition state that is responsible for the cleavage of the N–O bond and the creation of the Fe–O bond. The barrier height for this electronic process on the sextet potential energy surface was computed to be 18.8 kcal mol^{-1}; if we measure the activation energy from the dissociation limit, i.e., $Fe^+(^6D)$ and $N_2O(^1\Sigma^+)$, it amounts to 8.4 kcal mol^{-1}. This low activation energy is quite reasonable considering that the N–O bond dissociation energy for the reaction, $N_2O \rightarrow N_2 + O$, is only 39 kcal mol^{-1} in the gas-phase process.[26] The imaginary mode of vibration in the transition state indicates the forward reaction pathway for the decomposition of the N_2O molecule; thus, this transition state is confirmed to correctly connect the reactant complex and the products.

We now have useful information on the reaction pathway and the energetics for the N_2O decomposition leading to iron-oxo species that are responsible for the hydroxylation of methane[12] and of benzene.[13] A schematic representation for the catalytic cycle for the methane–methanol and benzene–phenol conversions is shown in Fig. 2. Direct evidence for the presence of such an iron(III)-oxo species has not yet been provided in Fe-ZSM-5 zeolite; however, an iron(III) species was actually detected from Mössbauer measurements.[27] We think that an iron-oxo species should be formed upon decomposition of N_2O on the AlO_4 surface site of ZSM-5 zeolite.

Possible Models of "α-Oxygen" on Zeolite. Having described the reaction pathway and the energetics for the formation of the bare FeO^+ complex and the catalytic cycle for the gas-phase methane–methanol and benzene–phenol conversions, let us now consider how "α-oxygen" is generated on the surface of Fe-ZSM-5 zeolite. Panov, Shilov, Shteinman, and their collaborators[27] recently suggested that "α-oxygen" should be analogous to the diiron core structure of soluble methane monooxygenase (sMMO), which has been proposed by Münck, Lipscomb, Que, and their collaborators[28] to involve an $Fe_2(\mu\text{-}O)_2$ diamond core. The underlying reason for such a proposal[27] to "α-oxygen" remains unclear to us, but such a suggestion may be an interesting working hypothesis because "α-oxygen" and sMMO have very similar catalytic functions. We do not intend to rule out the possible dinuclear models for "α-oxygen",[27] but from our previous work[13,14] a mononuclear iron-oxo model may be sufficient for the purpose of discussing a possible reaction mechanism for the methane–methanol and benzene–phenol conversions by the surface oxygen species of Fe-ZSM-5 zeolite.

The gas-phase reaction cycle presented in Fig. 2 is probably the key to understanding the catalytic reaction that takes place over Fe-ZSM-5 zeolite. If a coordinatively unsaturated iron-oxo species is present at a catalytically active center, our mechanistic proposals[12,13] indicated in Scheme 1 can be applied to hydrocarbon hydroxylation catalyzed by

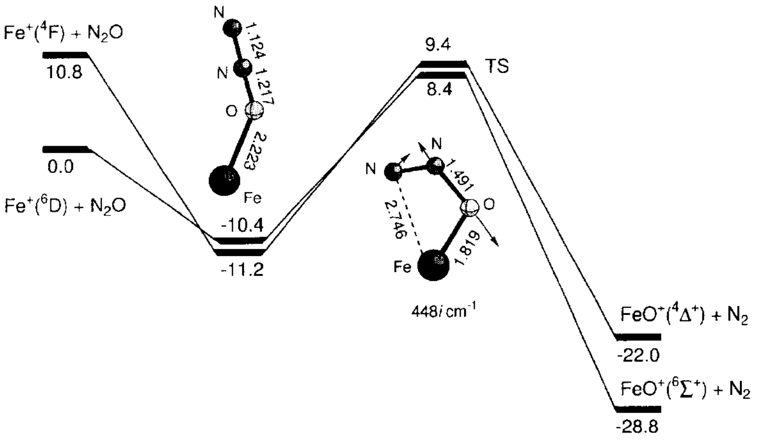


Fig. 1. Potential energy diagrams for the formation of the FeO^+ complex in the sextet and the quartet states. Relative values indicated are in kcal mol^{-1}. Optimized structures of the sextet state are shown. Bond lengths are in Å.

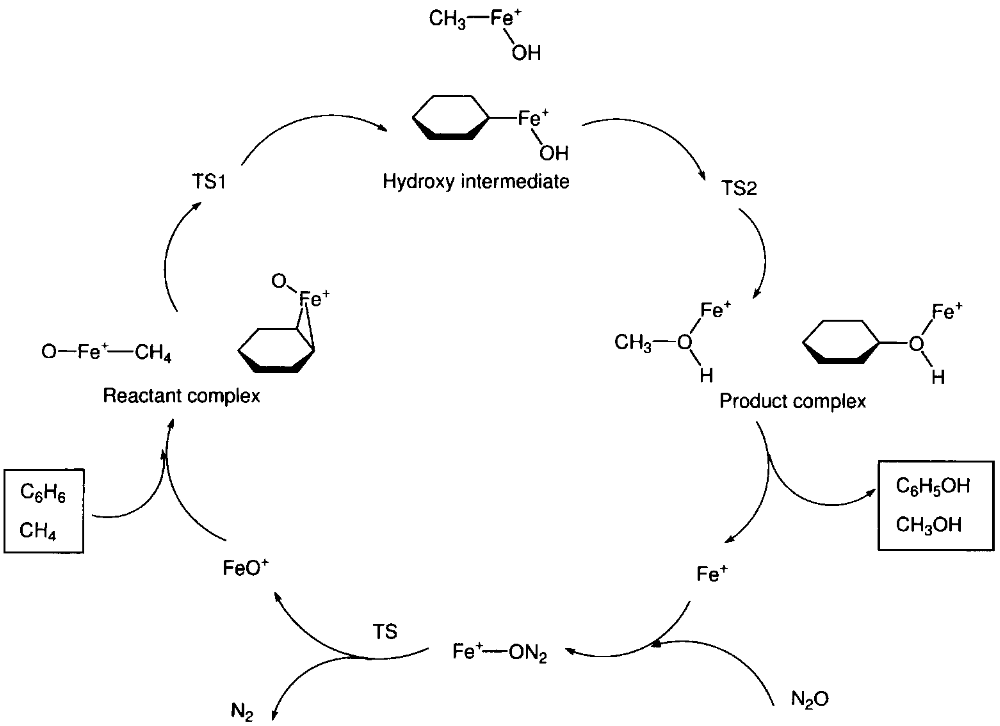


Fig. 2. A proposed catalytic cycle for the methane–methanol and benzene–phenol conversions by the FeO^+ complex.

transition-metal complexes. The ground state of the FeO^+ complex, the formal charge of the iron atom being +3, is a sextet spin state. A high-spin iron(III) species was actually detected in the active form of Fe-ZSM-5 zeolite from an analysis of Mössbauer hyperfine parameters,[27] and therefore the reactive iron species at the catalytic center is probably a high-spin iron(III) species. Direct comparison between the gas-phase reaction and the catalytic reaction over Fe-ZSM-5 zeolite may be difficult because important ligand effects are not included in our analyses for the gas-phase reaction. However, we believe that the essential features of the two reactions are identical, while the detailed energetics can, of course, be affected by differences in coordination spheres of the transition-metal active center.

To the best of our knowledge, there is no detailed structural information on transition metals supported on zeolite, particularly concerning whether such metal active centers are isolated or assembled. Kucherov and Slinkin[29] concluded from ESR measurements that supported Cu, Cr, and Fe cations should be located in non-lattice (surface) positions of ZSM-5 zeolite. Analyses on the active center of Cu-ZSM-5 zeolite,[30,31] which exhibits an important catalytic function of NO_x decomposition such as $2NO \rightarrow N_2+O_2$,[32] have been carried out using reasonable zeolite models. Taking the general features of zeolite[33] into account and on the basis of these previous studies,[29—31] we set up a model for the iron active site of ZSM-5 zeolite, as indicated in Chart 1. The Fe active center located on the AlO_4 surface site may be coordinated by water molecules in the resting state under ambient conditions, and they can be removed by heat treatment. We have carried out DFT computations of the decomposition of N_2O over this hypothetical model complex indicated in Chart 1.

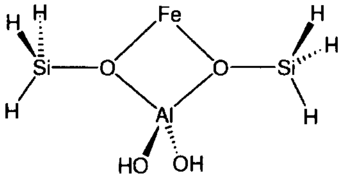


Chart 1.

We present in Fig. 3 a computed reaction pathway for the formation of a possible iron-oxo species that models "α-oxygen". Single-point calculations using the optimized sextet geometries confirmed that the sextet potential energy surface should lie below the quartet potential energy surface. Therefore the total charge of the model active site, $FeAl(OSiH_3)_2(OH)_2$, is neutral. We considered only the sextet state for the computational analyses because of the detailed considerations of the corresponding gas-phase reaction discussed above. The proposed reaction pathway and the energetics in Fig. 3 are essentially identical to those of the gas-phase reaction, $Fe^+ + N_2O \rightarrow FeO^+ + N_2$, presented in Fig. 1. Dinitrogen oxide is strongly bound to the iron active site of the cluster model, the binding energy being 29.8 kcal mol^{-1} at the B3LYP level. A computed activation energy for the decomposition of N_2O is only 2.4 kcal mol^{-1} and the transition state lies well below the dissociation limit (-27.4 kcal mol^{-1}), so the decomposition of N_2O is expected to readily occur on the active site of Fe-ZSM-5 zeolite. The energetics is slightly different from that of the gas-phase reaction. This difference arises from the contrast between the initially formed complexes; the dissociating O–N distance is 1.217 Å in the $Fe^+(N_2O)$ complex and 1.404 Å in the zeolite-model complex.

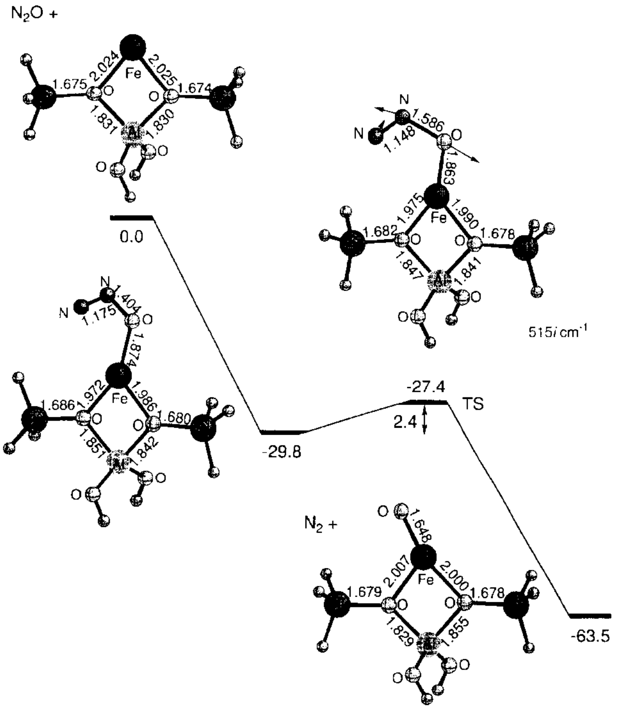


Fig. 3. A potential energy diagram for the formation of "α-oxygen" on Fe-ZSM-5 zeolite in the sextet state. Relative values indicated are in kcal mol^{-1}. Bond lengths are in Å.

We show in Chart 2 possible models of "α-oxygen" on Fe-ZSM-5 zeolite. We assumed a three-coordinate iron in the DFT computations demonstrated above, but four- or even five-coordinate iron is also possible in that the metal active center is coordinatively unsaturated. We think that water molecules may coordinate to the iron active center of Fe-ZSM-5 zeolite under ambient conditions, as indicated at the right in Chart 2, but these water molecules may be desorbed when the metal center is catalytically active. If a coordinatively unsaturated iron-oxo species is generated, it should become a reaction center that affords a coordination site for methane, benzene, and other hydrocarbon molecules. We think that multinuclear models are also possible if the iron active site is coordinatively unsaturated. Our two-step concerted mechanism in Scheme 1 should play a role in the hydroxylation of methane and of benzene on such metal active sites. In a future paper,[34] we will present the detailed reaction pathways and the energetics on the direct hydroxylation of methane and of benzene that occur on our model of "α-oxygen" indicated in Fig. 3.

Oxygen Exchange in Iron-Oxo Species. Oxygen exchange at the "α-oxygen" center of Fe-ZSM-5 zeolite has been investigated using $^{18}O_2$. According to Panov and collaborators,[7a,7d] the isotope exchange indicated in reaction (5) takes place at the "α-oxygen" center at room temperature. The bracketed oxygen species in this reaction stands for "α-oxygen" that is highly reactive toward methane and benzene. The activation energy for the isotope exchange occurring on Fe_2O_3 was measured to be 28 kcal mol^{-1}.[7d]

$$(^{16}O) + {}^{18}O_2 \rightarrow (^{18}O) + {}^{16}O^{18}O \qquad (5)$$

In the context of the discussion described above, we consider that the unknown structure of "α-oxygen" should have close relevance to a coordinatively unsaturated iron-oxo species. If this proposal is valid, we must demonstrate that the oxygen-exchange reaction takes place reasonably well on the bare FeO^+ complex; we thus carried out a reaction-path analysis for the isotope exchange of reaction (5). As shown in Fig. 4, this reaction is initiated by the coordination of O_2 to the iron active center to form peroxo species. There are well-known coordination modes for dioxygen; one is an end-on mode, and the other is a side-on mode. The two peroxo species in Fig. 4 are connected by a transition state, the barrier height of which is 4.2 and 6.6 kcal mol^{-1} depending on the starting points; therefore the two binding modes are likely to be easily interconverted at room temperature. The computed reaction pathway for the exchange of the oxygen atom in the FeO^+ complex is connected by the two $(O_2)FeO^+$ peroxo species and the four-membered cyclic intermediate. Only half of the reaction shown in this illustration is sufficient for the description of this exchange reaction because it is symmetric in respect of the four-membered cyclic intermediate. The other transition state connects the side-on peroxo species and the reaction intermediate, the $Fe(O_3)$ skeleton of which has a C_{2v} geometry. The activation energy for this transition state is computed to be 37.4 kcal mol^{-1} measured from the side-on peroxo species and 27.5 kcal mol^{-1} measured from the dissociation limit; thus this is likely to be a rate-determining step for the oxygen-exchange reaction.

It is interesting to compare the two $(O_2)FeO^+$ species shown in Fig. 4. The computed Mulliken charge of the dioxygen in the side-on complex is -0.16 and, surprisingly, that in the end-on complex is $+0.06$. Thus, we cannot use "peroxo" for describing these two $(O_2)FeO^+$ species anymore from the viewpoint of the computed Mulliken charges. However, Mulliken charge is usually different from formal charge; for example, the computed Mulliken charge of the oxygen atom in the FeO^+ complex is -0.4 while its formal charge is -2. The charge shift in the side-on complex results in a slight increase in the O–O distance because the antibonding π^* orbitals are partly occupied. However, since the magnitude is small, the O–O distance of 1.289 Å is not

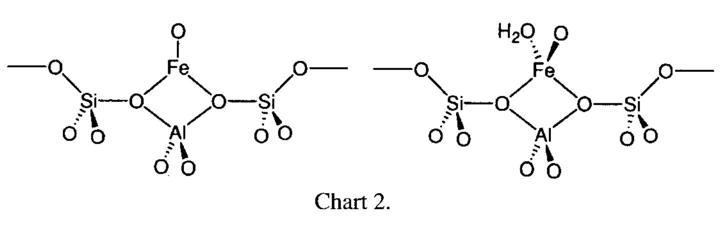


Chart 2.

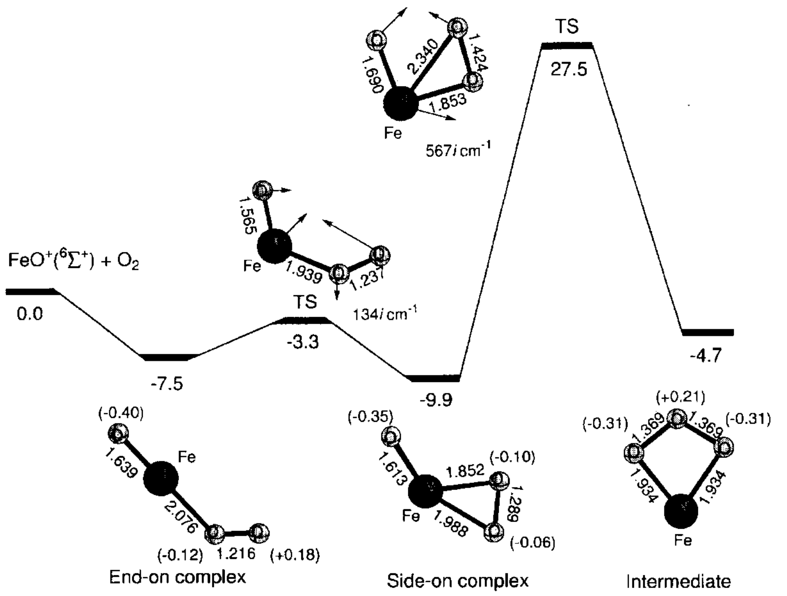


Fig. 4. A potential energy diagram for the oxygen exchange on the FeO^+ complex of the sextet state. The values in the parentheses are computed Mulliken charges.

so long compared to 1.4 Å, a typical value for metal-bound peroxo species. As expected and computed, the O–O distance in the end-on complex remains unchanged from that of neutral dioxygen.

Finally we refer to the oxygen exchange on Fe-ZSM-5 zeolite. Figure 5 presents a computed energy diagram and optimized structures of the reaction intermediates and the transition states along the reaction pathway for the oxygen exchange. We confirmed from single-point calculations that the sextet potential energy surface should lie below the quartet potential energy surface. The side-on complex is formed in the initial stage of the reaction, the binding energy being 18.2 kcal mol^{-1}. The computed Mulliken charge of the dioxygen in the side-on complex is −0.46 and the optimized O–O distance is 1.310 Å; thus, the O–O distance is proportional to the amount of electron transfer. Although we could not find an end-on "peroxo" complex, the general features of this reaction are identical to those of the gas-phase reaction in Fig. 4. We therefore do not repeat similar discussions, but we should state one thing; the activation barrier for the oxy-

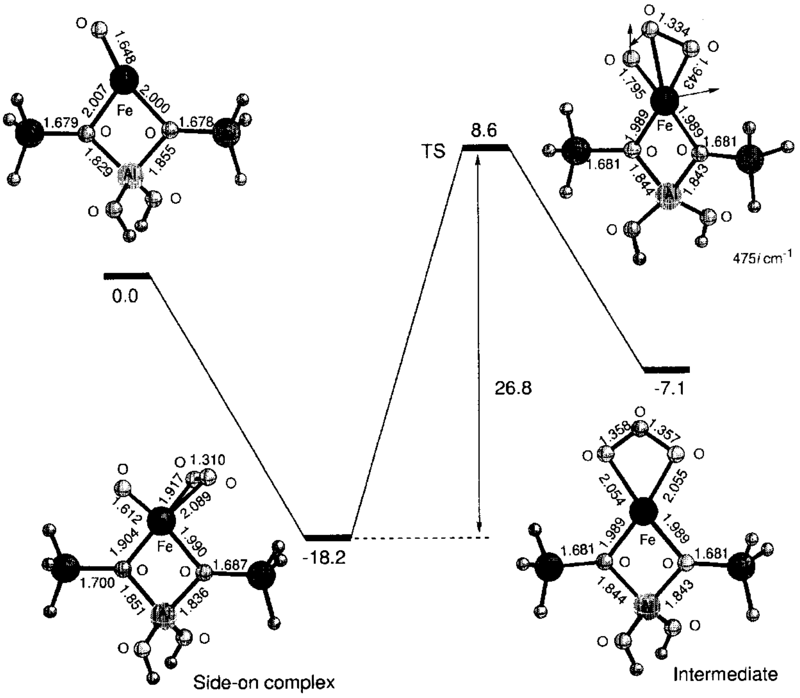


Fig. 5. A potential energy diagram for the oxygen exchange on "α-oxygen" of Fe-ZSM-5 zeolite in the sextet state.

gen exchange is 26.8 kcal mol^{-1} measured from the peroxo complex.

Conclusions

We proposed a possible mechanism for the formation of the bare FeO^+ complex and "α-oxygen" on Fe-ZSM-5 zeolite from the decomposition of dinitrogen oxide (N_2O). In the initial stages of the reactions, complexes involving an $Fe(ON_2)$ moiety are formed in both cases. The activation energies for the decomposition of N_2O in the gas phase and on a possible iron active site model of Fe-ZSM-5 zeolite are computed to be 19.6 and 2.4 kcal mol^{-1}, respectively. Judging from the small activation energy from the zeolite model, the decomposition of N_2O is expected to easily take place at a coordinatively unsaturated iron active center, leading to an iron-oxo species. The iron-oxo species thus formed on the AlO_4 surface site of ZSM-5 zeolite should play an essential role in the direct hydroxylation of methane, benzene, and other hydrocarbons. The oxygen exchange on the iron-oxo complexes was also computed and analyzed. The activation energies for the oxygen exchange on the bare FeO^+ complex and on the "α-oxygen" model were computed to be 37.4 and 26.8 kcal mol^{-1}, respectively. Our theoretical predictions are useful for the rational understanding of the transition-metal active centers on ZSM-5 zeolite and for the design of industrial catalysts that can directly hydroxylate methane, benzene, and other hydrocarbons.

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