

Oxidation of Ethane to Ethanol by N₂O in a Metal-Organic Framework with Coordinatively Unsaturated Iron(II) Sites

Long, J.R., *et al.*, *Nat. Chem.* **2014**, *6*, 590.

Mechanism of Oxidation of Ethane to Ethanol at Iron(IV)-Oxo Sites in Magnesium-Diluted Fe₂(dobdc)

Gagliardi, L.; Truhlar, D. G. *et al.*, *J. Am. Chem. Soc.* **2015**, *137*, 5770.

1. Introduction

1-1. Oxidation of alkanes into alcohols

- An established process of oxidation of alkanes into alcohols is important as an alternative to compressed natural gas for storage or transportation of fuels.
- In nature, selective C-H oxidation is carried out by copper and iron metalloenzymes.ⁱ
- As a synthetic system, iron-oxo complexes have been attracted much attention, but efficiency is low, and they are easy to decompose without protective protein.
- Tethering a molecular iron species to a porous solid support (e.g. silica, polystyrene, zeolites) could prevent decomposition (**Figure 1**).ⁱⁱ
- However:
 - 1) Formation of multiple iron species: many byproducts, difficult to characterize
 - 2) Low turnover number (~1).
 - 3) Other problems: steric crowding, site inaccessibility, metal leaching

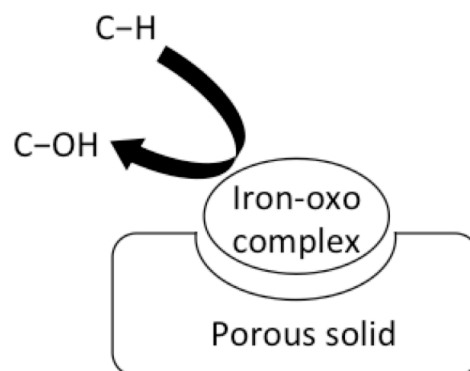
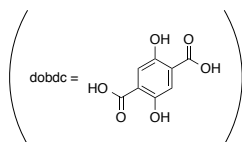


Figure 1. Oxidation by iron-oxo complex supported by porous solid

1-2. *This Work*: oxidation of ethane to ethanol by terminal iron(IV)-oxo moieties supported by metal-organic framework (MOF)

Advantages of metal-organic framework (MOF) as porous solid

- High surface area, porosity
- Chemical/thermal stability
- Synthetic tunability
- High crystallinity → suitable for characterization by single-crystal and/or powder-diffraction.
- Weak-field ligand (carboxylates and aryl oxides) → high-spin species (i.e. molecular iron(IV)-oxo complexes generally utilize nitrogen-based chelating ligands.)

Idea: Use Fe-MOF-74 ($\text{Fe}^{\text{II}}_2(\text{dobdc})$)

- Hexagonal channels of the framework are lined with a single type of square pyramidal iron (II) site (**Figure 2**).
- The high density and redox-active nature of the open metal sites engender excellent O_2/N_2 and hydrocarbon separation properties.ⁱⁱⁱ
- However, as for the reactivity of the framework, only the hydroxylation of benzene into phenol and the oxidation of methanol into formaldehyde have been reported.^{iv}

Hypothesis: Binding of N_2O forms highly reactive iron(IV)-oxo species??

(inspired by well established AlphOx process, in which zeolite and N_2O are used as an oxidation reaction of benzene to phenol).^v

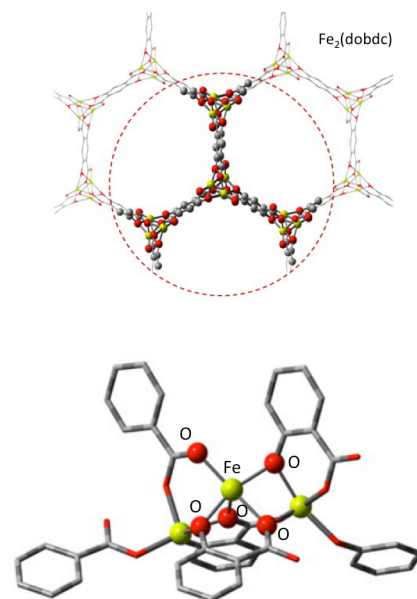


Figure 2. The cluster model of Fe-MOF-74

2. Results and Discussion (1): Oxidation Reaction

2-1. Experimental Procedure

- After heating a mixture of MOF, N_2O , and ethane at 75 °C for 24 h, ethanol and some byproducts were obtained (determined by ^1H NMR) (**Figure 3**, top scheme).

2-2. Optimization of MOF

- First, **Fe-MOF-74** ($\text{Fe}^{\text{II}}_2(\text{dobdc})$) was used as the framework, but many byproducts (acetaldehyde, diethylether and other ether oligomers) were obtained.

➔ overoxidation and oligomerization are due to the close proximity of reactive iron centres?

- Instead of **Fe-MOF-74**, the author used a mixed-metal MOF, $\text{Fe}_{0.1}\text{Mg}_{1.9}(\text{dobdc})$, in which iron(II) sites are diluted with redox-inactive magnesium(II) centres ➔ isolated iron centres
- Using $\text{Fe}_{0.1}\text{Mg}_{1.9}(\text{dobdc})$, the yield of ethanol was increased although small amount of acetaldehyde was also obtained.
- Investigation of surface area and unit-cell parameters showed formation of solid solution rather than a mixture of two separate phases.

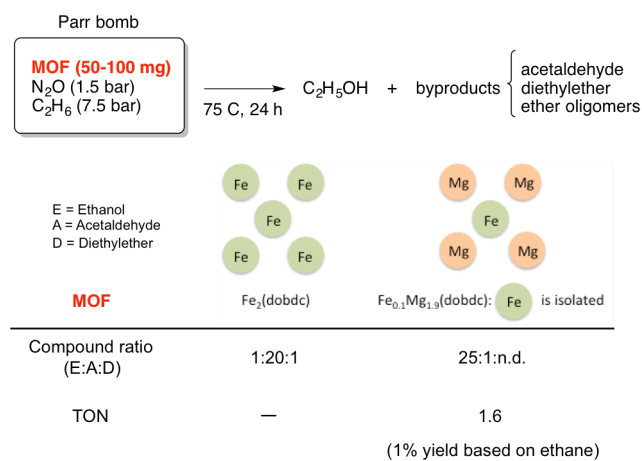


Figure 3. Schematic image of the oxidative experiment using MOF and the reactivity and selectivity of $\text{Fe}_2(\text{dobdc})$ and $\text{Fe}_{0.1}\text{Mg}_{1.9}(\text{dobdc})$.

3. Results and Discussion (2): Mechanistic Study

3-1. Backgrounds

High-spin iron(IV)-oxo complex

- It activates strong C-H bond.
- This state can be found in enzymatic catalysts.
- In contrast, synthesized mononuclear complexes tend to have low-spin.^{vi}
- Moreover, it is possible that spin-crossover occurs during the reaction.^{vii}

3-2. Overview of the reaction

- The proposed mechanism involves four key steps and seven intermediates (**Figure 4**).
- All the calculations were performed on a 26-atom mononuclear model (**Figure 5**).

3-3. Iron(IV)-Oxo formation

- N_2O binds to **A** yielding $\eta^1\text{-O}$ and $\eta^1\text{-N}$ isomers.
- The isomers have similar stabilities, and Neutron diffraction predicted coordination to favored (60%) over the $\eta^1\text{-N}$ coordination (40%) (**Figure 6**).
- N_2O is bound only weakly to iron(II) centres, and the interaction is fully reversible.
- $\eta^1\text{-O}$ coordination mode is followed by the formation of an iron(IV)-oxo intermediate **B**.
- DFT calculation shows that the iron(IV)-oxo intermediate is quintet state.
 → despite the strong-field ligand character of the oxo unit, the presence of five oxygen atom that come from dobdc^{4-} linker enforces a weak ligand field at the Fe center.

3-4. C-H bond activation

- **B** interacts with ethane to form **C** (**Figure 7**).
- The abstraction of the H atom from ethane yields a iron(III)-hydroxo species with a nearby ethyl radical.

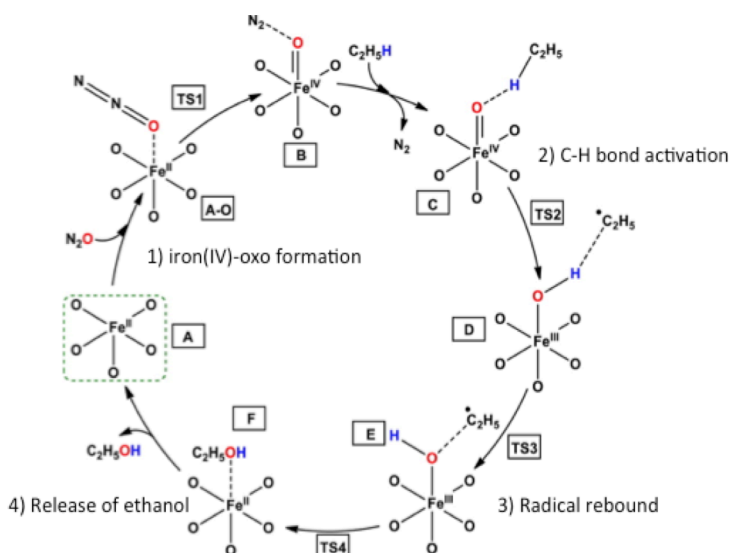


Figure 4. Proposed mechanism for the oxidation of ethane to ethanol in $\text{Fe}_{0.1}\text{Mg}_{1.9}(\text{dobdc})$

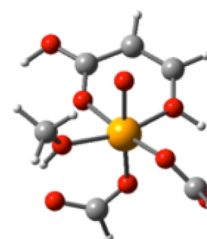


Figure 5. The 26-atom mononuclear model

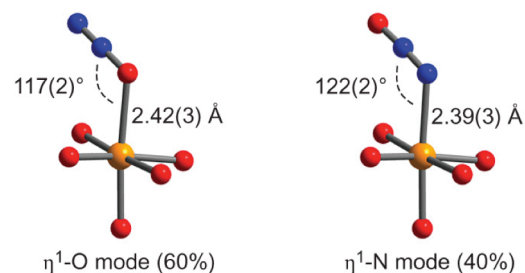


Figure 6. Experimental structures for N_2O binding

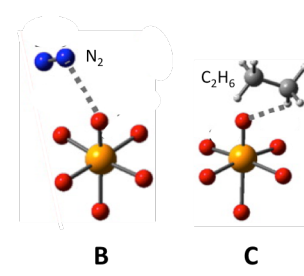


Figure 7. Optimized structure of **B** and **C**

3-5. Formation and release of ethanol

- This step involves the reaction of the iron(III)-hydroxo complex with the ethyl radical to form ethanol (**Figure 8**).
- The formation of **TS4** is preceded by a rotation of the hydroxo group along the Fe(III)-O axis in **D** to give **E** via **TS3**. Then a shift of the ethyl radical toward the Fe(III)-OH center occur.
- Torsional angle for **TS4** is about 105° , which enables the formation of ethanol from **TS4** and recovery of the Fe(II) active site.

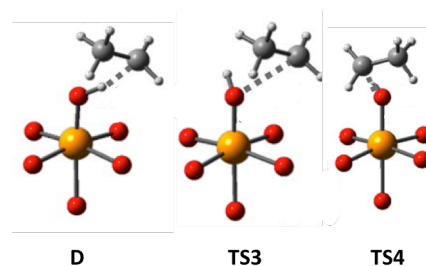


Figure 8. Optimized structure of **D**, **TS3**, and **TS4**.

3-6. Discussion throughout the catalytic cycle

- The ground spin state for the iron center of all the intermediate and TS were quintet, which was enabled by weak-field ligands.
- Crossing of the two spin surfaces does not occur at any point through the whole catalytic cycle.
- Calculation also revealed that other undesired pathways (i.e. dehydrogenation and dissociation) that can compete with the formation of ethanol were shown to involve higher barriers than the hydroxylation pathway.

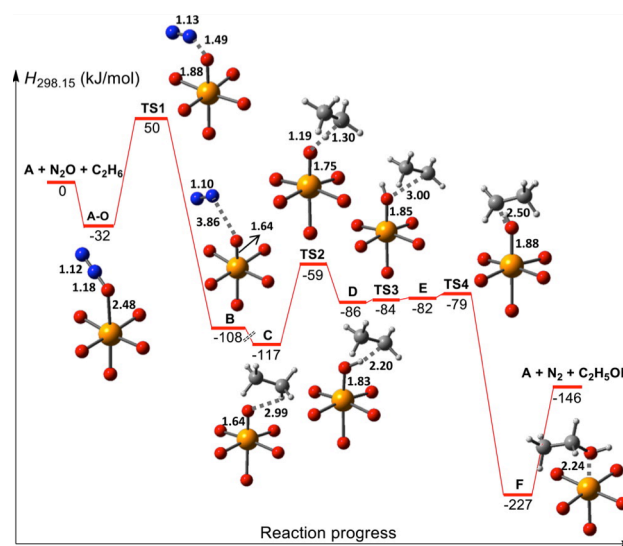


Figure 9. Enthalpy profile of the catalytic cycle

4. Conclusion

- $\text{Fe}_{0.1}\text{Mg}_{1.9}(\text{dobdc})$ and N_2O are able to form stable, crystalline, high-spin Fe(IV)-oxo species.
- The species activated ethane and convert it into ethanol in better efficiency and selectivity.
- Mechanistic study showed that all the intermediates and TS were high spin (quintet state).

5. References

- ⁱ a) Himes, R. A. *et al. Curr. Opin. Chem. Biol.* **2009**, *13*, 119. b) Costas, M. *et al. Chem. Rev.* **2004**, *104*, 939.
ⁱⁱ a) Watton, S. P., *et al. Prog. Inorg. Chem.* **2002**, *51*, 333.
 b) Leadbeater, N. E., *et al. Chem. Rev.* **2002**, *102*, 3217. c) Panov, G. I. *et al. React. Kinet. Catal. Lett.* **1997**, *61*, 251.
ⁱⁱⁱ Bloch, E. D. *et al. J. Am. Chem. Soc.* **2011**, *133*, 14814.
^{iv} a) Marcz, M. *et al. Micropor. Mesopor. Mater.* **2012**, *335*, 1606.
 b) Bhattacharjee, S. *et al. J. Nanosci. Nanotechnol.* **2010**, *10*, 135.
^v Notte, P.P. *Topics in catalysis*, **2000**, *13*, 387.
^{vi} Que, L., Jr. *Acc. Chem. Res.* **2007**, *40*, 493. ^{vii} Que, L., Jr. *J. Am. Chem. Soc.* **2006**, *128*, 8590.

-
- ⁱ a) Himes, R. A. *et al. Curr. Opin. Chem. Biol.* **2009**, *13*, 119. b) Costas, M. *et al. Chem. Rev.* **2004**, *104*, 939.
- ⁱⁱ a) Watton, S. P., *et al. Prog. Inorg. Chem.* **2002**, *51*, 333. b) Leadbeater, N. E., *et al. Chem. Rev.* **2002**, *102*, 3217. c) Panov, G. I. *et al. React. Kinet. Catal. Lett.* **1997**, *61*, 251.
- ⁱⁱⁱ Bloch, E. D. *et al. J. Am. Chem. Soc.* **2011**, *133*, 14814.
- ^{iv} a) Marcz, M. *et al. Micropor. Mesopor. Mater.* **2012**, *335*, 1606. b) Bhattacharjee, S. *et al. J. Nanosci. Nanotechnol.* **2010**, *10*, 135.
- ^v Notte, P.P. *Topics in catalysis*, **2000**, *13*, 387.
- ^{vi} Que, L., Jr. *Acc. Chem. Res.* **2007**, *40*, 493.
- vii