

Selective Binding of O₂ over N₂ in a Redox-Active Metal-Organic Framework with Open Iron(II) Coordination Sites

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1. Introduction

1-1. Separation of O₂ from air

- O₂ is the most widely used commodity chemical. For example, pure O₂ is required for the process of reducing CO₂ emission from power plant.
→ The method of separation of O₂ is required.
- Nowadays, the separation of O₂ from air is carried out using two methods.
 - (1) Cryogenic distillation process (based on the difference of boiling point)
→ Requirement of an enormous amount of energy
 - (2) Zeolites which absorb N₂ over O₂ (based on the difference of the size)
→ Poor selectivity
 - (3) New method: Based on the difference of interaction with metal?

1-2. Metal-organic frameworks for gas separation

- MOF has high surface area and open metal coordination sites
→ Effective interaction between oxygen and open metal sites is expected.
- MOF, whose metal cation site is exposed, such as M₂(dobdc) along with M₃(BTC)₂, can be generated by evacuation of frameworks.
- Previously, the authors showed that the coordinatively unsaturated Cr^{III} in Cr₃(BTC)₂ adsorbs O₂ over N₂ via charge transfer.
→ However, the interaction with O₂ proved too strong to achieve full reversibility (Figure 2).¹

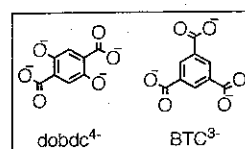


Figure 1.

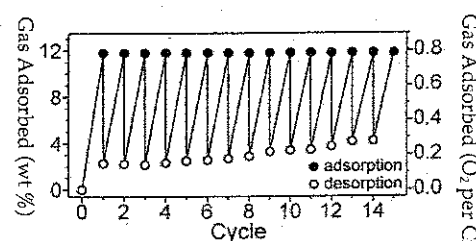


Figure 2.

1-3. This work

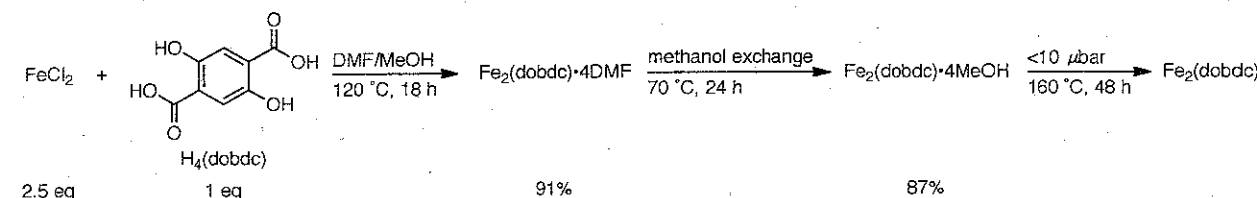
- In order to achieve full reversibility, Fe₂(dobdc) was synthesized and the ability of gas adsorption was investigated.
→ Fe^{II} is an obvious candidate in view of its widespread deployment as an O₂ carrier in biology.
- The mechanism of adsorption was revealed by Mössbauer spectroscopy and powder neutron diffraction.

2. Results and discussion

2-1. Synthesis and characterization of Fe₂(dobdc)

- First, solvated Fe₂(dobdc) was generated. After solvent exchange, Fe₂(dobdc) was obtained by removing solvent under dynamic vacuum at 160 °C (Scheme 1).

Scheme 1.



- X-ray diffraction revealed the structure like the honeycomb (Figure 3).
- Surface area was measured by low-pressure N₂ adsorption as 1360 m²/g.
→ This value was close to that of desolvated MOF, such as Ni₂(dobdc) (1218 m²/g) and Co₂(dobdc) (1341 m²/g).
→ This data indicates the full elimination of solvent and the existence of coordinatively unsaturated open iron sites.

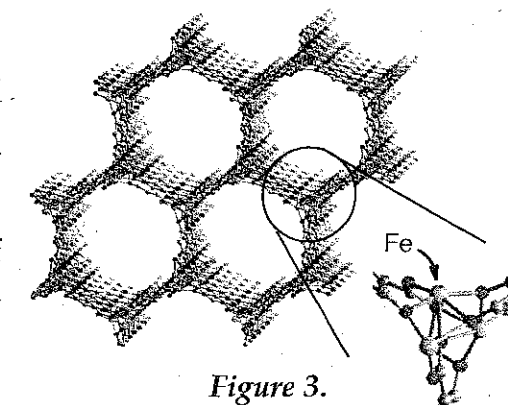


Figure 3.

2-2. O₂ and N₂ adsorption

2-2-1 At room temperature

- Strong binding of O₂ to Fe^{II} centers was observed and the adsorption isotherm reached near 9.3 wt % at 1 bar (Figure 4).
→ 0.5 O₂ molecules per iron center (at 0.01 bar)

- O_2 adsorption / N_2 adsorption = 7.5
→ The highest selectivity among the reported MOF

- However, O_2 adsorption was found to be irreversible, that is, desorption was not achieved.

2-2-2 At low temperature (211 K)

- Adsorption isotherm reached to 18.2 wt %, and was found to be reversible (Figure 5).
→ 1.0 molecules per iron center (at 0.1 bar)
- O_2 adsorption / N_2 adsorption = 11.4
→ Full reversible adsorption of O_2 was achieved.

2-3. Mössbauer spectra

The different O_2 adsorption at different temperatures suggests the existence of two different modes by which O_2 binds to the open iron sites.

→ Mössbauer spectroscopy was employed to probe the electronic structure (Figure 6).

2-3-1 Low temperatures

- At 94 K, isomer shift was between that of high-spin Fe(II) and that of high-spin Fe(III).

→ High spin $Fe^{II/III}$ with partial electron transfer to form weak bond with O_2 was generated ($Fe_2(O_2)_2(dobdc)$).

2-3-2 High temperatures

- As temperature was increased, spectra changed and indicated that the formation of high-spin Fe^{III} .

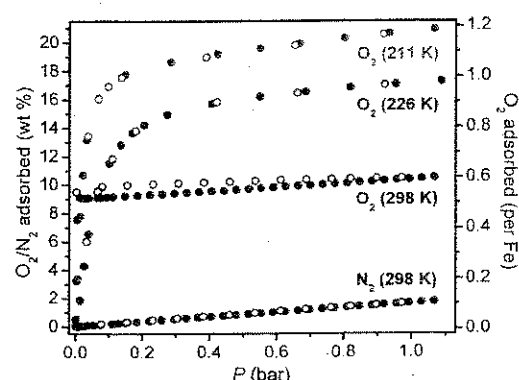


Figure 4.

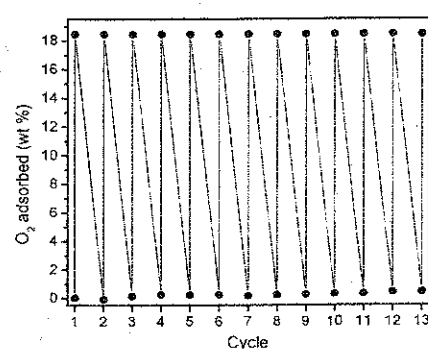


Figure 5.

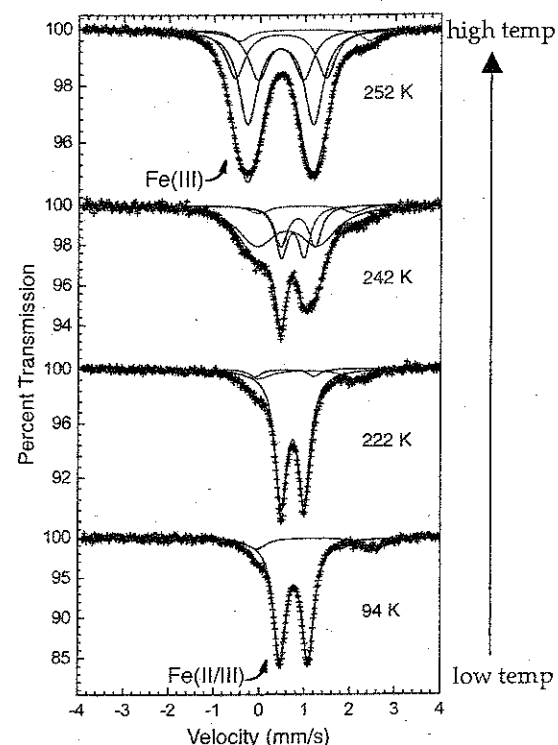


Figure 6. ($Fe_2(dobdc) + O_2$ at various temperatures)

- In addition, this spectra was superposition of at least two different spectra of iron(III)

→ It was assumed that there are two different iron centers, with O_2^{2-} and without O_2^{2-} .

→ By heat, an activation barrier is overcome for the electron transfer from two different iron centers to form a bound peroxide anion.

2-4. Structure via neutron powder diffraction (Figure 7)

(A) At 100 K, O_2 binds in a symmetric side-on coordination mode and O-O separation of 1.25(1) Å lies between free O_2 (1.2071(1) Å) and O_2^- unit (1.28 Å).

→ This result is consistent with only partial reduction of O_2 .

(B) At room temperature, O_2 binds in an asymmetric side-on coordination mode and O-O separation of 1.6(1) Å is consistent with peroxide, O_2^{2-} .

→ Two-electron reduction occurred.

(C) In the case of N_2 , although there is N_2 -framework interaction, the metal-specific interaction is much weaker than those for O_2 .

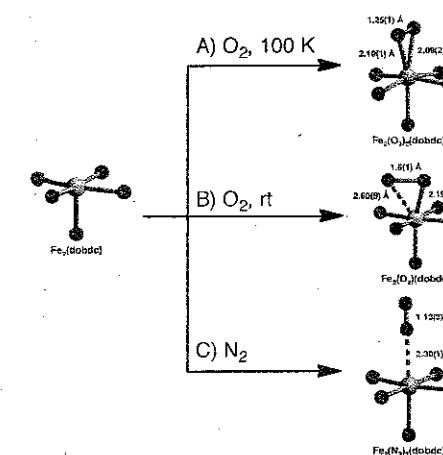


Figure 7.

3. Conclusions

- The ability of $Fe_2(dobdc)$ to selectively bind O_2 over N_2 was demonstrated.
- At 226 K, reversible adsorption of O_2 was achieved, and it was caused by partial reduction of O_2 by the electron transfer from Fe.
- At room temperature, the adsorption of O_2 is irreversible. It is because the second electron transfer occurs and results in formation of peroxide anion.

4. References

(1) Murray, L. J.; Dinca, M.; Yano, J.; Chavan, S.; Bordiga, S.; Brown, C. M.; Long, J. R. *J. Am. Chem. Soc.* 2010, 132, 7856–7857.