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Separating Air Using Metal-Organic Frameworks: Influence of the MOF Metal on Oxygen and Nitrogen Binding Energies

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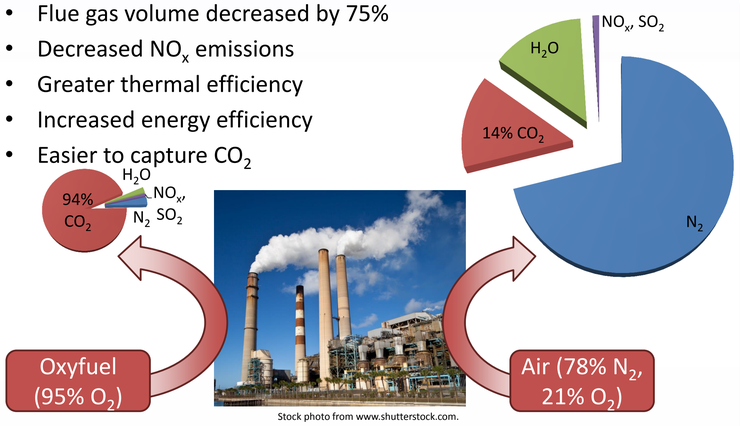
Oxyfuel for cleaner power plants

Benefits of using **oxyfuel** in power plants[1]

- Flue gas volume decreased by 75%
- Decreased NO_x emissions
- Greater thermal efficiency
- Increased energy efficiency
- Easier to capture CO_2

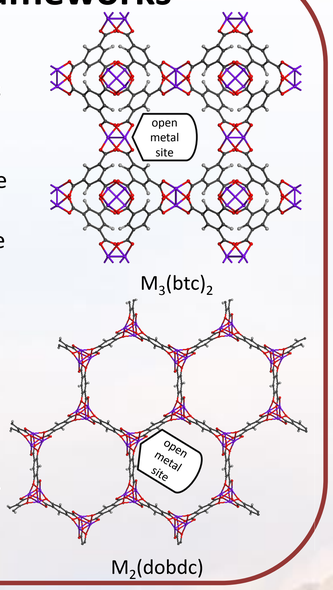


The generation of **oxygen-enriched air** is currently done by cryogenic distillation, an energy-intensive and expensive process.[2]

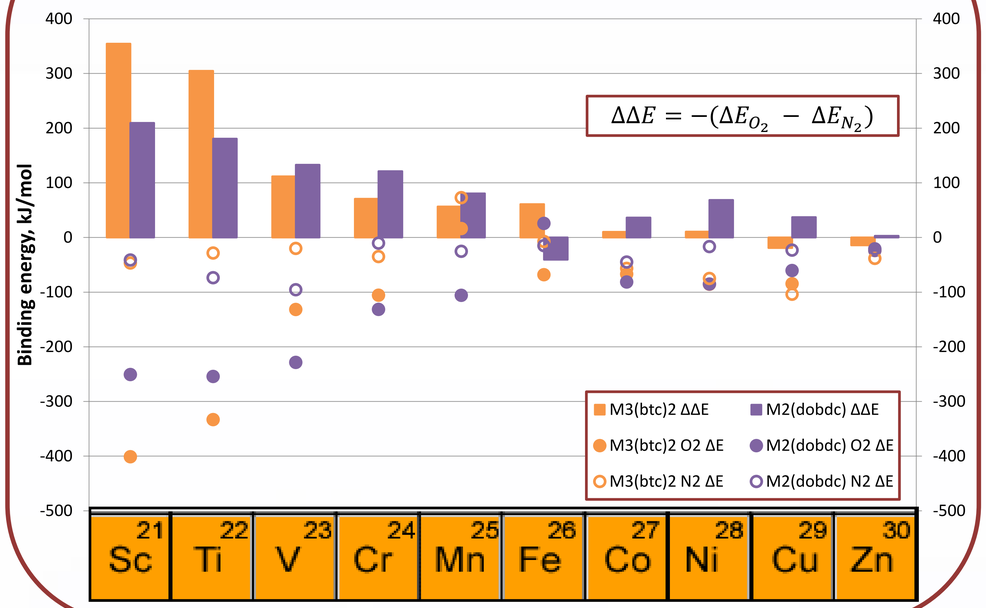
Metal-organic frameworks

Metal-organic frameworks (MOFs) are porous solids consisting of metal clusters connected by multidentate organic linkers, connected to form a three-dimensional extended network.[3] Because of their extremely high specific surface areas (up to 6000 $m^2 \cdot g^{-1}$),[3] MOFs are able to adsorb and store great amounts of adsorbates with possible applications in the separation of small molecules like oxygen.

MOFs with **open metal sites** are particularly suited to separating oxygen from nitrogen, based on differences in bonding and electronic properties rather than size or shape.[4]



Binding energy as a function of metal



Bonding geometry as a function of metal

Bonding geometries of oxygen binding to $M_3(btc)_2$ variants

Metal (M)	Bonding Mode*	M-O Distance (Å)†	O-O Distance (Å)	M-O-O Angle (°)
Sc	Side-on	1.91	1.49	67
Ti	Side-on	1.85	1.46	67
V	Linear	1.71	1.29	174
Cr	Side-on	1.98	1.32	71
Mn	Bent	1.86	1.29	120
Fe	Bent	1.97	1.28	118
Co	Bent	1.93	1.27	126
Ni	Bent	1.95	1.26	118
Cu	Bent	2.34	1.24	118
Zn	Bent	2.27	1.24	119

Bonding geometries of nitrogen binding to $M_3(btc)_2$ variants

Metal (M)	Bonding Mode*	M-N Distance (Å)†	N-N Distance (Å)	M-N-N Angle (°)
Sc	Bent	2.34	1.14	137
Ti	Bent	2.41 (nb)	1.13	127
V	Linear	2.28 (nb)	1.12	168
Cr	Bent	2.73 (nb)	1.12	159
Mn	Bent	2.44	1.12	127
Fe	Linear	1.96	1.13	177
Co	Linear	1.95	1.12	175
Ni	Linear	1.99	1.12	172
Cu	Bent	2.34 (nb)	1.12	146
Zn	Linear	2.22	1.11	167

Bonding geometries of oxygen binding to $M_2(dobdc)$ variants

Metal (M)	Bonding Mode*	M-O Distance (Å)†	O-O Distance (Å)	M-O-O Angle (°)
Sc	Side-on	1.93	1.47	68
Ti	Linear	1.73	1.31	170
V	Linear	1.71	1.29	169
Cr	Bent	1.84	1.31	121
Mn	Bent	1.88	1.30	118
Fe	Bent	2.04	1.30	123
Co	Bent	1.84	1.29	119
Ni	Bent	1.95	1.27	122
Cu	Bent	2.35	1.25	119
Zn	Bent	2.28	1.26	116

Bonding geometries of nitrogen binding to $M_2(dobdc)$ variants

Metal (M)	Bonding Mode*	M-N Distance (Å)†	N-N Distance (Å)	M-N-N Angle (°)
Sc	Linear	2.36	1.12	168
Ti	Linear	2.07	1.14	177
V	Linear	1.98	1.14	175
Cr	Linear	1.88	1.14	177
Mn	Bent	2.34	1.12	135
Fe	Bent	3.59 (nb)	1.12	152
Co	Linear	1.93	1.13	179
Ni	Bent	2.92 (nb)	1.12	116
Cu	Bent	2.92 (nb)	1.12	132
Zn	Linear	2.64 (nb)	1.12	173

* Side-on bonding mode corresponds to M-X-X angle 67°-71°; Bent bonding mode corresponds to M-X-X angle 94°-159°; Linear bonding mode corresponds to M-X-X angle 165°-179°.

† (nb) indicates that the M-X interatomic distance is too long to represent a bonding interaction.

Methods

Initial structures of MOFs were prepared by substituting the metals in $Cu_3(btc)_2$[5] and $Zn_2(dobdc)$[6] with each of the first-row transition metals, resulting in **twenty different MOFs** for study.

Plane wave density functional theory (DFT) calculations were performed on periodic structures of each MOF in the Vienna ab initio simulation package (**VASP**)[7] with the Perdew-Burke-Ernzerhof (**PBE**) functional[8] including dispersion corrections (**DFT-D2**)[9] Geometries were optimized and **static binding energies (ΔE_{O_2}, ΔE_{N_2})** were calculated by

$$\Delta E_{O_2} = E_{MOF+O_2} - E_{MOF} - E_{O_2}$$

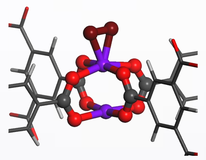
The **differences in binding energies ($\Delta\Delta E$)** for oxygen and nitrogen were calculated by

$$\Delta\Delta E = -(\Delta E_{O_2} - \Delta E_{N_2})$$

Bonding geometries

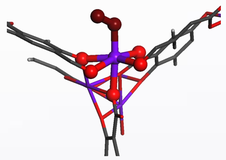
Bonding of O_2 and N_2 to the MOF metal can occur through three **bonding modes**: side-on, bent, and linear bonding.

Side-on bonding ∠M-X-X 67° - 71°



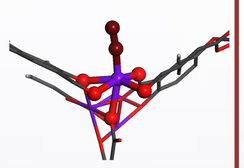
$Cr_3(btc)_2(O_2)$

Bent bonding ∠M-X-X 94° - 159°



$Mn_2(dobdc)(O_2)$

Linear bonding ∠M-X-X 165° - 179°



$Ti_2(dobdc)(O_2)$

Conclusions

- Oxygen binding energy (ΔE_{O_2}) is much **stronger for early transition metals** than mid or late transition metals.
- Nitrogen binding energy (ΔE_{N_2}) is **relatively weak** for all transition metals.
- **Oxygen bonding** can be side-on, bent, or linear.
- **Nitrogen bonding** is always bent or linear.
- **Side-on bonding** is associated with **stronger binding energy**.
- General **trends are consistent** for two different MOF structures: $M_3(btc)_2$ and $M_2(dobdc)$.
- **Metal matters!** To selectively adsorb oxygen over nitrogen, focus on **early transition metals**.

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