In Situ Insight into Reversible O$_2$ Gas-Solid Reactions

Christina Wegeberg*, a Andrew D. Bond, b Christine J. McKenzie a

aDepartment of Physics, Chemistry and Pharmacy, University of Southern Denmark, Odense M 5230, Denmark
bDepartment of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom.

e-mail: wegeberg@sdu.dk

A Stepwise Gas-Solid Reaction

Crystal Co Co O

N t Bu N N O

3+

Co Co O

N t Bu N N O

2+

NH$_2$

O

3+

O2

O2

NO$_3$-

O2

NO$_3$-

O2

NO$_3$-

Semi-Oxy

Deoxy

A series of crystalline solids containing cationic tetracobalt complexes spontaneously chemisorb O$_2$ from the air.[1] The sorption/desorption of O$_2$ is reversible and selective and occurs without the material losing its (single) crystallinity over several cycles.[2-4]

Phase Tweaking Overrides Molecular Tweaking

In the solid state the O$_2$ binding affinity is influenced strongly by the phase and counter anion, this is in contrast to solution state where the introduction of electron withdrawing groups on the co-ligands strongly affects O$_2$ affinity[5-8].

An obstacle race for O$_2$: The gas cell experiment indicates the presence of a transient conduit through the crystals of the non-porous nitrate salt.

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The gas-solid single crystal to single crystal transformation[4] shows that one nitrate per dioxygen moves 5-7 Å in the crystal lattice concomitant with O$_2$ sorption and release. The deoxy form contains nitrate anions bridging the dicobalt(II) sites[3].

Work in Progress

- Insight into the O$_2$ sorption/desorption of other phases to investigate the role of non-coordinating counter anions
- Gas-solid reactions with other gasses (NO and H$_2$)
- Light triggered release of O$_2$?