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In Situ Insight into Reversible O₂ Gas-Solid Reactions

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A Stepwise Gas-Solid Reaction

Crystal

Oxy form of 1(NO₃)₄

Deoxy form

O₂

heat

O₂

A series of crystalline solids containing cationic tetracobalt complexes spontaneously chemisorb O₂ from the air.[1] The sorption/desorption of O₂ is reversible and selective and occurs without the material losing its (single) crystallinity over several cycles.[2-4]

Crystals that Breathe

Phase Tweaking Overrides Molecular Tweaking

In the solid state the O₂ 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 O₂ affinity.[5,6]

An obstacle race for O₂:
The gas cell experiment indicates the presence of a transient conduit through the crystals of the non-porous nitrate salt.

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 O₂ sorption and release. The deoxy form contains nitrate anions bridging the dicobalt(II) sites[3].

Work in Progress

- Insight into the O₂ sorption/desorption of other phases to investigate the role of non-coordinating counter anions
- Gas-solid reactions with other gases (NO and H₂)
- Light triggered release of O₂?

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Packaging of deoxy form of 1(NO₃)₄

Counter anions are removed to show conduits

Oxygen desorption of 1(X)₄

Selective gas sorption for 2(PF₆)₄

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The gas-cell setup at the synchrotron DIAMOND (beamline I19) enables crystallographic evidence that the reaction proceeds via a semi-oxy, thus we have detected two steps in the chemisorption process[3].

As vacuum (10⁴ bar) is applied, the ellipsoids of one of O₂ are enlarged significantly.

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