Shades of red: Selective oxidation with molecular oxygen.

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Selective oxidation of organic molecules is the Catch-22 of catalysis. Oxygen is freely available, but its high kinetic barrier means that once it is activated, you get high reactivity and low selectivity.[1] There are three traditional solutions to this problem: *(i)* Work at low conversions. This engineering solution is practical, but it means large recycle streams and low per-pass yields. *(ii)* Use a peroxide, such as H_2O_2, peracetic acid or *t*-BuOOH instead of oxygen.[2] This also works, but it costs an extra reagent. *(iii)* Use a platinum catalyst. Hmmm... true, platinum can activate O_2, but it's too expensive for many large-scale applications.

Yet there is a fourth way: some catalytic surfaces can donate an electron to the antibonding orbital in the oxygen molecule, creating a "peroxide-like" active species *in situ*. In the lecture, I will show how to make these materials and control their surface parameters. [4–6] I will then show how this active species can be generated and how it is applied in the selective oxidation of alcohols using cooperative cascade catalysis.[6]

[1] Comparative autoxidation of 3-carene and α-pinene: Factors governing regioselective hydrogen abstraction reactions. G. Rothenberg, Y. Yatziv and Y. Sasson, *Tetrahedron*, **1998**, 54, 593.

[2] Copper-catalyzed homolytic and heterolytic benzylic and allylic oxidation using *tert*-butyl hydroperoxide. G. Rothenberg, L. Feldberg, H. Wiener and Y. Sasson, *J. Chem. Soc., Perkin Trans.* 2, **1998**, 2429.

[3] A simple synthesis of an N-Doped carbon ORR Catalyst: Hierarchical micro/meso/macro porosity and graphitic shells. D. Eisenberg, W. Stroek, N. J. Geels, C. S. Sandu, A. Heller, N. Yan and G. Rothenberg, *Chem. Eur. J.*, **2016**, 22, 501.

[4] A rational synthesis of hierarchically porous, N-doped carbon from Mg-based MOFs: Understanding the link between nitrogen content and oxygen reduction electrocatalysis. D. Eisenberg, W. Stroek, N.J. Geels, S. Tanase, M. Ferbinteanu, S.J. Teat, P. Mettraux, N. Yan and G. Rothenberg, *Phys. Chem. Chem. Phys.*, **2016**, 18, 20778.

[5] The evolution of hierarchical porosity in self-templated nitrogen-doped carbons and its effect on oxygen reduction electrocatalysis. D. Eisenberg, P. Prinsen, N.J. Geels, W. Stroek, N. Yan, B. Hua, J.-L. Luo and G. Rothenberg, *RSC Adv.*, **2016**, 6, 80398.

[6] Cooperative catalysis for selective alcohol oxidation with molecular oxygen. T.K. Slot, D. Eisenberg, D. van Noordenne, P. Jungbacker and G. Rothenberg, *Chem. Eur. J.*, **2016**, 22, 12307.

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