

Tuning the reactivity of high-valent nickel oxidants for hydrocarbon oxidation

Prasenjit Mondal,^a Paolo Pirovano,^a Ankita Das,^a Erik R. Farquhar,^b Marcel Swart,^c Aidan R. McDonald^{*a}

Addresses list: ^aSchool of Chemistry and CRANN/AMBER Nanoscience Institute, Trinity College Dublin, The University of Dublin, College Green, Dublin 2, Ireland; ^bCase Western Reserve University Center for Synchrotron Biosciences, National Synchrotron Light Source II, Brookhaven National Laboratory II, Upton, NY 11973, USA; ^cICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain and Institut de Química Computacional i Catalisi; Universitat de Girona, Facultat de Ciències, Campus Montilivi, 17003 Girona, Spain.

e-mail: aidan.mcdonald@tcd.ie

High-valent terminal metal-oxygen adducts are hypothesized to be the potent oxidising reactants in late transition metal oxidation catalysis. In particular, examples of high-valent terminal nickel-oxygen adducts are sparse, meaning there is a dearth in the understanding of such oxidants. Herein we describe the preparation of a family of high-valent Ni oxidants. Electronic absorption, electronic paramagnetic resonance, and X-ray absorption spectroscopies, and density functional theory calculations have been used to probe the electronic and structural properties of these compounds. Structure function relationships in a series of complexes have been elucidated, providing us with critical insight into the reactivity properties of high-valent nickel oxidants.¹⁻³

- 1 P. Pirovano, E. R. Farquhar, M. Swart, A. J. Fitzpatrick, G. G. Morgan, A. R. McDonald, *Chem. Eur. J.*, **2015**, *21*, 3785-3790;
- 2 P. Pirovano, E. R. Farquhar, M. Swart and A. R. McDonald, *J. Am. Chem. Soc.*, **2016**, *138*, 14362-14370.
- 3 P. Mondal, P. Pirovano, A. Das, E. Farquhar, A. R. McDonald, submitted **2017**