



Activation of molecular oxygen on metal oxides

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Activation of molecular oxygen on the surface of metal oxides is of fundamental importance in heterogeneous catalysis. Control over occurrence and distribution of various activated oxygen species on the surface of oxide catalysts is the key issue in terms of achieving high selectivity to specific selective oxidation products and the abatement of total combustion to undesired CO₂ in alkane oxidation.



Experimentally observed correlations between performance and charge carrier dynamics give hints to universal design concepts of high-performance catalysts for selective oxidation. Catalysts with high selectivity at almost complete alkane conversion (VPP and MoVTeNb M1 oxide) reveal the property of a “buffer” for charge carriers in its bulk that can be transported to the active sites when the delivery of redox equivalents between adsorbed species is too slow. Likewise, the surface layer containing the active sites is robust against chemical changes induced by the lack of redox equivalents leading to chemical oxidation or reduction of the sites.^{1,2}

Surface molecular aspects of oxygen activation are studied at different temperatures and gas-phase compositions by Raman spectroscopy combined with DFT calculations. Phonon calculations were performed using Quantum Espresso 5.4.0 to refine the band assignment of the V₂O₅ Raman spectrum with the aim to allow a clear identification of the specific oxygen species that undergo exchange.³ Labelling experiments with ¹⁸O₂ show that the type of oxygen in V₂O₅, which is exchanged, strongly depends on gas composition and temperature. High temperatures are required under oxidizing conditions and the vanadyl oxygen is the only species that is exchanged at 580°C, whereas in the presence of propane and oxygen all types of oxygen (vanadyl and bridging) are exchanged. Oxygen vacancies generated by propane in the surface region facilitate the incorporation of gaseous oxygen into the lattice of V₂O₅. Under normal reaction conditions of alkane oxidation (400 – 420 °C), mainly vanadyl oxygen O1 is involved in oxygen exchange.³ The experiments demonstrate that spectroscopic analysis of the working catalyst is needed for generating insight that is causally related to the catalytic phenomena. Currently, various oxidation catalysts are studied using the same methodology.⁴

¹A. M. Wernbacher, M. Eichelbaum, T. Risse, S. Cap, A. Trunschke, R. Schlögl, *The Journal of Physical Chemistry C* **2019**, *123*, 8005.

²A. M. Wernbacher, P. Kube, M. Hävecker, R. Schlögl, A. Trunschke, *The Journal of Physical Chemistry C* **2019**, *123*, 13269.

³Y. Wang, in preparation.

⁴T. Fu, Y. Wang, A.M. Wernbacher, R. Schlögl, A. Trunschke, *ACS Catalysis* **2019**, *9*, 4875-4886.