

# Catalysis Science of Oxidation Reactions by Mixed Metal Oxides

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Mixed metal oxides (e.g., bulk mixed metal oxides, polyoxoanion metalates (POMs), supported metal oxides, metal oxide-containing molecular sieves and zeolites, and supported metal oxides) find wide application as oxidation catalysts. Recent molecular-level characterization studies have revealed that all these disparate mixed metal oxide catalyst systems contain similar catalytic metal oxide active sites at their surfaces. Both bulk mixed metal oxides and supported metal oxides possess similar surface metal oxide sites. For example, surface  $\text{MoO}_x$  species are the catalytic active sites for methanol oxidation to formaldehyde for both bulk  $\text{Fe}_2(\text{MoO}_4)_3$  and supported  $\text{MoO}_x$  catalysts. Similarly, propane oxidation to propylene and propylene oxidation to acrolein can be performed by similar surface metal oxide sites. Metal oxide-containing molecular sieves and zeolites also possess similar surface metal oxide species as supported metal oxides. For example, V-silicalite and supported  $\text{VO}_x/\text{SiO}_2$  exhibit the same TOF and selectivity for methanol oxidation to formaldehyde.

In light of the above findings that similar metal oxide catalytic active sites are present at surfaces of mixed metal oxides, the catalytic roles of the bulk mixed oxide phases must be addressed in a new light. One common characteristic of oxidation reactions by mixed metal oxides, bulk as well as supported metal oxides, is that the reaction rates are almost universally zero-order in partial pressure of  $\text{O}_2$ . This indicates that all mixed metal oxide catalysts follow a Mars-van Krevelen reaction mechanism where the rate-determining-step involves lattice oxygen, bulk as well as surface, and reoxidation of surface metal oxide catalytic active sites with  $\text{O}_2$  is a fast step and not a rate-determining-step. Consequently, the reaction kinetics are always dependent on the partial pressure of the reactants (either first- or half-order), but not on the oxygen partial pressure. Given that supported metal oxides and bulk mixed metal oxides both rapidly reoxidize their surface metal oxide active sites, transport of bulk lattice oxygen to the surface of bulk mixed metal oxides is not a distinguishing characteristic for oxidation catalysts. There is, however, exchange of surface oxygen with lattice oxygen taking place for bulk mixed oxides, but this occurs on a longer time scale and is not necessarily related to the Mars-van Krevelen mechanism involving the surface metal oxide active sites.

The bulk lattice of bulk mixed metal oxide catalysts, however, can have several positive effects on the active surface metal oxide sites. For example, the bulk lattice phase is a metal oxide reservoir that can supply active metal oxides to replace volatile metal oxide components. This is especially important for Mo oxide-containing oxidation catalysts that readily lose active surface Mo oxide via volatilization. The crystalline bulk mixed oxide phase may also act as an oxide support with a unique surface structure for the active surface metal oxide phase. This seems to be the case for n-butane oxidation over the crystalline vanadyl pyrosulfate phase consisting of bulk  $\text{V}^{+4}/\text{P}^{+5}$  that supports a surface layer of  $\text{V}^{+5}/\text{P}^{+5}$  active sites.

The presentation will elaborate upon these and other examples of oxidation catalysis.

## Biography of Israel E. Wachs

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In a career spanning three decades, Prof. Wachs has earned international renown for research into heterogeneous catalysis.

His research focuses on the catalysis science of mixed metal oxides (supported metal oxides, bulk metal oxides, polyoxometalates, zeolites and molecular sieves) for numerous catalytic applications (selective oxidation for manufacture of value-added chemicals, environmental catalysis (selective catalytic reduction of NO<sub>x</sub> and SO<sub>x</sub>), hydrocarbon conversion by solid acid catalysts for increased fuel energy content, olefin metathesis for on demand production of scarce propylene, olefin polymerization, conversion of methane to liquid aromatic fuels, biomass pyrolysis, water-gas shift for production of clean hydrogen and photocatalytic splitting of water to clean hydrogen).

The research aims to identify the catalytic active sites present on the heterogeneous catalyst surface to allow establishment of fundamental structure-activity/selectivity relationships that will guide the rational design of advanced catalysts. The research approach taken by the Wachs group is to simultaneously monitor the surface of the catalyst with spectroscopy under reaction conditions and online analysis of reactant conversion and product selectivity with online GC/mass spectrometer analysis. This new methodology has been termed operando spectroscopy and is allowing for the unprecedented development of molecular level structure-activity/selectivity relationships for catalysts. The spectroscopic techniques employed by the Wachs group for determination of the catalytic active sites and surface reaction intermediates are Raman, infrared (IR), ultra violet- visible (UV-vis), X-ray Absorption Spectroscopy (XANES/EXAFS), Nuclear Magnetic Resonance (NMR), Electron Paramagnetic Resonance (EPR) and Temperature Programmed Surface Reaction (TPSR). Isotopic labeling of Deuterium, Oxygen-18 and Carbon-13 is also used to track reaction pathways, determine rate-determining-steps and distinguish between spectator species and actual surface reaction intermediates.

The U.S. Environmental Protection Agency has honored Wachs with a Clean Air Excellence award for a catalytic process he invented that converts paper-mill pollutants into formaldehyde. The American Chemical Society (ACS) has given Wachs the [George A. Olah Award](#) for achievements in hydrocarbon and petroleum chemistry and the American Institute of Chemical Engineering (AIChE) has honored Wachs with the Catalysis and Reaction Engineering Division Practice Award. He is the recipient of multiple awards from local catalysis societies (Michigan, New York, Chicago and Philadelphia). In 2011, he was named a Fellow of the [American Chemical Society \(ACS\)](#), the highest honor bestowed by the society. In 2012, he was recognized by the German Alexander von Humboldt Foundation with a Humboldt Research Award and the International Vanadium Chemistry Organization with its Vanadis award.

Wachs has published more than 300 highly cited technical articles (H index of 80) and holds more than three dozen patents. Additional details about the Wachs group activities (publications, presentations, awards, etc.) can be found on the group site ([lehigh.edu/operando](http://lehigh.edu/operando)).