As the pressure and materials gaps between real catalysis and traditional UHV single crystals studies are narrowing, experiments and modelling that straddle both sides of the gap appear essential to understand surface properties and functions of catalysts. Producing well defined (experimental and theoretical) model systems of practical catalysts such as alumina supported vanadia is challenging because of the complexity of the real systems The aggregates' structure and the nature of the support in particular, are important because both relate to the (real) catalysts activity for partial oxidation reactions; however, they are not fully understood. Experimental model systems of VOx/Al2O3 catalysts had been produced. Their thorough experimental study yielded some puzzling results on the particles' surface termination, and pointedly left the VOx/Al2O3 vibrational properties a matter of great debate. I will discuss theoretical models which include the clean and oxygen defective V2O5(001) surface, as well as vanadia aggregates on α-Al2O3(0001), κ-Al2O3(001) and an ultrathin alumina film on NiAl(110). These case studies were investigated using density functional theory-based calculations and statistical thermodynamics. Highlights of the results are the prediction of a missing-row vanadyl (O=V) oxygen defect structure at the V$_2$O$_5$(001) surface under reducing conditions and of the facile surface reduction along the [010] oriented rows; a phenomena that has been experimentally confirmed. The assignment of vibrational spectra will also be addressed. Both the experimental and theoretical model studies have resulted in relevance on a deep level. They challenge the view generally accepted in the real world of powder samples, in which vibrational spectroscopy is routinely used for catalyst characterization. Taking into account an important aspect of the complex systems functionality, i.e., their reducibility, structure-reactivity relationships will be discussed.