New Insights into Catalytic Reactions on Metal Oxide Surfaces from Computer Modeling

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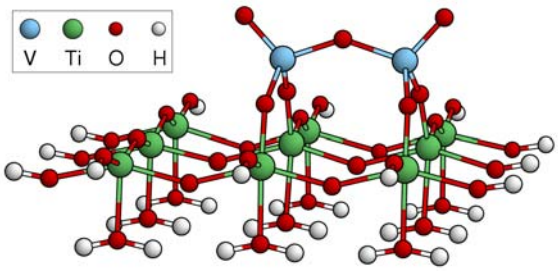
Selective catalytic oxidation is a very promising, yet poorly understood, technology for chemical and fuels processing. Obtaining a molecular understanding of catalysis is a key to being able to control the selectivity and activity of new catalysts and can significantly reduce energy requirements in the chemical industry. State-of-the-art computer simulations are now an attractive complement to experiment in exploring the mysteries of catalysis. We have been using density functional calculations to understand, in detail, the pathway(s) by which hydrocarbon molecules are catalytically transformed both by dehydrogenation and oxygenation including which features of catalyst and catalyst-support architecture and electronic structure are key to the selective creation of C-O and to the activation of C-H bonds.

We have discovered how a substrate activates small metal oxide clusters to transform propane to propene, a key industrial process that requires much energy. In these computational studies of oxidative dehydrogenation of propane we have used density functional theory to assess different pathways involving stepwise adsorption of the propane, at an oxygen site followed by desorption of a water molecule and subsequent adsorption of an oxygen molecule to complete the catalytic cycle. Large barriers for this reaction are found for an isolated small vanadium oxide cluster. The reaction barriers are found to be much lower when the small vanadium oxide clusters are attached to a titanium oxide surface. The calculations have provided an explanation for how the interface between the titanium oxide surface activates the small metal oxide cluster so that the reaction pathway is lowered in energy. We find that addition of the substrate serves to stabilizes a higher electronic state of the small metal oxide cluster, which is more reactive towards the removal of hydrogens from propane, i.e. the dehydrogenation catalysis reaction. With this knowledge, in future work, computer simulations will be used to help researchers develop new and improved catalysts for selective oxidation reactions.



Vanadia cluster on TiO_2 substrate

P. C. Redfern, P. Zapol, M. Sternberg, S. P. Adiga, S. A. Zygmunt, and L. A. Curtiss, *Journal of Physical Chemistry*, B 110 8363 (2006).