

MODELING CHEMICAL REACTIVITY: EFFECTS OF CONFINEMENT

Keith E. Gubbins and Erik Santiso
*Center for High Performance Simulation (CHiPS) and
Department of Chemical Engineering, North Carolina State University,
Raleigh, NC 27695, USA*

A goal of theory is to predict chemical reactivity – equilibrium composition, reaction mechanisms and reaction rates, as well as diffusion limitations – from first principles. At present our ability to achieve this is quite limited, for a number of reasons. First, *ab initio* methods are necessary, since electrons are rearranged, but these are computationally very demanding, and with current supercomputers we are quite limited in the length and time scales that can be accessed; moreover, the scaling of the computational burden with the number of electrons is poor. Second, reaction events are rare, and so even if we have the energy landscape for the reaction conventional molecular dynamics simulations are insufficient. A brief review of the most widely used methods to model chemical reactions, at both the electronic and atomistic levels will be presented, with comments on their applicability and a description of their strengths and weaknesses¹. In many applications a combination of *ab initio* and semi-classical atomistic simulations will be needed. Specialized atomistic simulation methods are usually necessary, since the reactions are themselves rare events, and the free energy landscape for the reaction is often rugged with many possible reaction paths.

Chemical reactions are often carried out in nano-structured materials, which can enhance reactions due to their large specific surface area, their interactions with the reacting mixture and confinement effects. An experimental investigation of the role of each possible catalytic effect is challenging, since experimental measurements reflect an integration over multiple catalytic effects. In this talk several of the different factors that can influence a chemical reaction in confinement will be considered. We first consider the influence of steric hindrance on the equilibrium and kinetics for the rotational isomerizations of several small hydrocarbons. These examples illustrate how reaction rates can vary doubly exponentially with the dimensions of the confining material (the 'shape-catalytic' effect). As a second example, we consider the unimolecular decomposition of formaldehyde on graphitic carbon pores of various sizes¹. These results illustrate the influence of electrostatic interactions with the supporting material on the reaction mechanism and equilibrium yield for reactions involving a charge transfer. As a final example, we consider the interaction of a water molecule with a defective carbon substrate as an example of a chemical interaction that can be enhanced through a shape-catalytic effect. We show using *ab initio* calculations how a vacancy site on a carbon surface can induce the thermal splitting of water at relatively low temperatures². We also examine the dissociation on a vacancy site on a nanotube surface, which shows the shape-catalytic effect of the surface curvature.

These results are a first step toward the design of catalytic materials that take advantage of different enhancing effects simultaneously.

¹ E. Santiso and K.E. Gubbins, “Multi-Scale Molecular Modeling of Chemical Reactivity”, *Molecular Simulation*, **30**, 699-748 (2004).

² M. Kostov, E.E. Santiso, A.M. George, K.E. Gubbins and M. Buongiorno Nardelli, “Catalytic role of defective carbon substrates in the dissociation of water”, *Physical Review Letters*, **95**, 136105 (2005).

¹ Erik E. Santiso, Aaron M. George, Keith E. Gubbins, Marco Buongiorno-Nardelli, *J. Chem. Phys.*, submitted (2006).

² M.K. Kostov, E.E. Santiso, A.M. George, K.E. Gubbins, M.B. Nardelli, *Phys. Rev. Lett.* **95** (2005) 136105.