

Catalysis within confined microenvironment modified by solvents: a revisit to traditional chemistries at solid-liquid interfaces

Hui Shi

Interest in liquid-phase reactions over heterogeneous catalysts is growing/reviving rapidly. In a renewable energy context, the driving force for this transition in processing paradigm comes from the urgency to create efficient conversion pathways for transforming biomass-derived feedstocks. The low volatility of many biomass-derived compounds renders their transport in the gas phase extremely challenging; as a result, catalysts must be able to operate, at moderately elevated temperatures, in the presence of aqueous or organic solvents or mixtures thereof. Heterogeneous catalysts can interact strongly with solvents and may undergo profound and even possibly irreversible changes in their structure, catalytic activity, and selectivity due to interfacial adsorption and/or reactions with solvent molecules. Nevertheless, our fundamental understanding of reactivity at “buried” solid–liquid interfaces is still much less developed compared to our knowledge about gas–solid catalytic reactions. Mechanistic analogies can, in some cases, be drawn between gas-phase and liquid-phase catalysis, but design criteria for catalysts and processes are generally not guaranteed to be transferrable from one to the other.

This talk will illustrate several key aspects of this paradigm shift mainly within microporous aluminosilicate zeolites, a well-established versatile catalytic entity that features locally ordered, three-dimensional confined microenvironment containing relatively uniform inherent acid strength. Most examples discussed in this talk concern seemingly simple chemistries, primarily, elimination of water from (chain and cyclic, primary and secondary) alcohols and electrophilic aromatic substitution between phenolics and alcohols/olefins. Using these examples, I will demonstrate that the consequences of solvent and solvation come in different forms: (1) the active acid center in a zeolite can change its nature to partially delocalized proton-solvent clusters (e.g., intraporous hydronium ions in contact with aqueous phase); (2) the stability, mobility and ordering of reactive intermediates and transition states can be dramatically altered by solvent molecules, affecting in turn the overall energy landscape and catalytic rates along a given pathway; and (3) the susceptibility of the material against deactivation and structural degradation may be altered. These consequences are discussed in terms of kinetics, mechanism and energetics, through the combination of experimental and theoretical assessments.