Pyrolysis of Organic Molecules Immobilized on Silica Nanoparticles: Impact of Surface Confinement on Reaction Mechanisms

A. C. Buchanan, III
Chemical & Analytical Sciences Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee

Abstract

The impact of confined spaces, such as the pores of zeolites, on chemical reaction pathways continues to draw considerable attention. However, to investigate such perturbations on high temperature (275-450 C) reactions, which are relevant to the pyrolysis of cross-linked fuel materials, requires the use of a more robust mode of surface confinement or the use of polymers. We have been examining the pyrolysis of fuel model compounds covalently attached to the surface of nonporous silica nanoparticles. The surface modification chemistry involves condensation of phenols or alcohols with surface silanols. The thermally robust Si-O-C_{aryl} tether to the silica surface permits the study of pyrolysis reaction kinetics and mechanisms up to temperatures approaching 550 C. However, since the tether can be cleaved by aqueous base, surface-attached pyrolysis products are easily recovered for quantitative analysis. In this presentation, the synthesis and characterization of silica-attached molecules will be described, and pyrolysis behavior will be compared with that in fluid phases. Diffusional constraints have been found to result in reduced rates of radical termination reactions on the surface, enhancement of radical pathways involving neophyl-like rearrangements, and enhancement of cyclization-dehydrogenation pathways. Furthermore, studies of two-component surfaces, designed to incorporate spacer molecules of varying structure, have revealed the ability of spacer molecules to act as molecular walls that hinder hydrogen transfer steps on the surface, or as participants in facile hydrogen transfer, radical relay steps resulting from the molecular organization on the surface. The implications of these results for fuel processing will also be mentioned.