

The research took advantage of our capabilities to perform in-situ and operando Raman spectroscopy on complex systems along with our developing expertise in the synthesis of uniform, supported metal oxide materials to investigate relationships between the catalytically active oxide composition, atomic structure, and support and the corresponding chemical and catalytic properties. The project was organized into two efforts:

*1) Synthesis of novel catalyst materials by atomic layer deposition (ALD).*

*2) Spectroscopic and chemical investigations of coke formation and catalyst deactivation.*

ALD synthesis was combined with conventional physical characterization, Raman spectroscopy, and probe molecule chemisorption to study the effect of supported metal oxide composition and atomic structure on acid-base and catalytic properties. Operando Raman spectroscopy studies of olefin polymerization leading to coke formation and catalyst deactivation clarified the mechanism of coke formation by acid catalysts.

Highly uniform submonolayer to multilayer thin films of titanium dioxide supported on high surface area silica gel have been synthesized by atomic layer deposition (ALD) using titanium tetrachloride ( $\text{TiCl}_4$ ) and titanium isopropoxide (TTIP) as metal precursors. The deposition rate of titania films from  $\text{TiCl}_4$  was found to be stable in the 150-300 °C temperature range which is slightly higher than that from TTIP at 150 °C. UV-vis DRS shows that the coordination geometry of Ti cations depends on the number of ALD cycles and the precursor but is essentially independent of deposition temperature. Using DRIFTS and visible Raman spectroscopy with pyridine as a probe molecule all the titania films studied were found to exhibit Lewis acidity but only films containing either chloride or carbonyl impurities possessed Brønsted acid sites. Additionally, three new pronounced bands in the Raman spectra,  $\nu_{6b}$  ( $638\text{ cm}^{-1}$ ),  $\nu_{9a}$  ( $1200\text{ cm}^{-1}$ ) and  $\nu_2$  ( $3103\text{ cm}^{-1}$ ), provide strong spectroscopic evidence for Brønsted acid sites on the surface. This research was published as “Surface Acidity and Properties of  $\text{TiO}_2/\text{SiO}_2$  Catalysts Prepared by Atomic Layer Deposition: UV-visible Diffuse Reflectance, DRIFTS, and Visible Raman Spectroscopy Studies”. *J. Phys. Chem. C* **2009**, *113* (28), 12412-12418.

The conversion of ethylene and propylene absorbed in zeolite H-MFI was studied using UV-Raman spectroscopy. In order to observe early-stage reaction intermediates, an infrared laser was

used as a fast heating source. Alkyl substituted naphthalenes and fluorenes, which have been previously suggested as hydrocarbon pool species, were observed regardless of the olefin reagent. Conjugated dienes were formed from propylene but not observed for ethylene at short reaction times. Conventional heating in a furnace was used to force the reaction to completion. For propylene sheet-like polyaromatic hydrocarbons were formed immediately. For ethylene cyclic dienes, conjugated olefins and ultimately sheet-like polyaromatic hydrocarbons were formed at progressively higher reaction temperatures. The results show that the polyaromatic species implicated as deactivating coke in zeolite catalysts can be formed by conversion of polyenes. This research was published as “Time-Resolved Studies of Ethylene and Propylene Reactions in Zeolite H-MFI by In-Situ Fast IR Heating and UV Raman Spectroscopy”. *ACS Catalysis* **2012**, 2 (11), 2424-2432.