63a Oxidative Dehydrogenation of Lower Alkanes over Oxide Catalysts Using N2o as an Oxidant

Matthew P. Woods, Chang Liu, Rick B. Watson, and Umit S. Ozkan

The chemical industry relies heavily on unsaturated hydrocarbons as feedstock for many industrially significant processes. The oxidative dehydrogenation (ODH) of lower alkanes, which has received much attention in recent years, offers many benefits compared to traditional production of unsaturated hydrocarbons by steam cracking and direct dehydrogenation. Despite substantial research on olefin production by ODH, major obstacles remain. Obtaining high selectivities towards alkenes is the greatest challenge.

The oxidative dehydrogenation of lower alkanes is believed to proceed via a Mars-van-Krevelen redox mechanism on metal oxide catalyst systems. During reaction, the catalyst surface is reduced as surface oxygen atoms abstract hydrogen from alkane molecules, ultimately forming olefins and water. Gas phase oxygen then adsorbs to the surface and undergoes a series of electron transfer processes before being incorporated back into the lattice, restoring the working oxidation state of the catalyst. When in equilibrium with the gas phase, the surface is populated by a number of short lived oxygen species, including O_2^- and O^-.

Clearly, in order to understand the ODH of lower alkanes, it is necessary to understand the role of lattice and gas phase oxygen. Alternate oxidants provide a means to investigate the role of oxidation-reduction processes occurring during ODH reactions. Novel oxidants offer a unique opportunity to tune the oxidation state of the catalyst and to study the role of surface oxygen in the ODH of lower alkanes.

Silica-titania supported molybdenum catalysts were tested in the ODH of ethane and propane using O_2 and N_2O as oxidants. ODH reactions using different alkane to oxidant ratios were also performed. Catalyst performance was characterized using a variety of techniques, including temperature programmed oxidation, X-ray photoelectron spectroscopy and diffuse reflectance IR spectroscopy.

Reaction performance under different oxidants depends heavily on which alkane is used (ethane of propane). Additionally, the ratio of alkane to oxidant influences the reaction performance. Steady state reactions with N_2O showed improved performance in ethane ODH. Ethene yield increased with decreasing alkane to N_2O ratio. Propane ODH followed an opposite trend. As alkane to N_2O ratio was decreased, propane yield increased. Trends observed in reaction experiments will be discussed in terms of the insight acquired through detailed characterization studies.