ABSTRACT

The conversion of ethane and propane to liquid fuels is an invaluable process that will help bridge the energy gap from fossil fuels to renewable energy sources. The development of shale gas upgrading technology must be aggressively pursued in order to achieve this goal. This necessitates the discovery, development, and optimization of non-traditional catalysts for upgrading these light alkane species in a cost-effective manner.

In this thesis, two catalysts were studied for different reaction steps in light alkane upgrading: strong-metal support interaction (SMSI) catalysts were studied with a focus on improving dehydrogenation activity and γ-Al_2O_3 as a new, innovative type of Lewis acid catalyst for oligomerization. Strong metal-support interaction catalysts have shown to improve desired product selectivity at the cost of fractional rates due to active site coverage. The goal of the SMSI study was to determine if the active site coverage of metallic nanoparticles could be controlled to lower levels than previously reported in SMSI catalysts with the aim of improving the rate while maintaining high selectivity. 2Pd-XTi/SiO_2 (2 wt% Pd, X wt% Ti) SMSI catalysts were synthesized to control Pd nanoparticle coverage. Increasing the Ti loading from 0.1 to 1.0 wt% increased the surface coverage from 40 to 85% after 550 °C reduction. The SMSI overlayer was removed by oxidation at 350 °C and re-reduction at 200 °C. Increasing the reduction temperature from 300 to 550 °C increased the SMSI coverage from 10 to 85% depending on the Ti loading and temperature which is a significant improvement over the 70-95% coverages previously observed. Catalysts with excess coverage result in a decreased rate with no improvement on product selectivity. Lower coverages allow for rate and selectivity optimization. Reducing coverage can improve the rate without a significant loss to selectivity. The coverage at which this occurs will vary based on the catalyst and reaction network.

The goal of the second study was to identify the active sites for olefin oligomerization on γ-Al_2O_3 and to determine their density. XSr/Al_2O_3 (X wt% Sr) catalysts were synthesized to poison the active sites. There was a decrease in the propylene oligomerization conversion with increasing Sr loading with >95% conversion loss above 1 wt% Sr. Pyridine IR indicates only Lewis acid sites

on γ-Al_2O_3. There was a linear decrease in the intensity of the Lewis acid peaks in the IR spectra when increasing the Sr loading which correlates with the loss in propylene conversion suggesting that Lewis acid sites are the active site. The acid site density was calculated to be ~0.2 sites per nm^2 of γ-Al_2O_3. Lewis acid sites are not typical thought of as catalytic for many hydrocarbon reactions including olefin oligomerization. The techniques utilized in this work indicate that they are active. This opens opportunity to discover other Lewis acid catalysts which may be significantly more active. Discovery work to identify other Lewis acid catalysts, in particular single ion metals, is was also explored with unexpected and promising results.