ANOOP UCHAGAWKAR

FINAL DOCTORAL DEFENSE

CHEMICAL ENGINEERING

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CEBC, Bldg. B, Room 104

Research Advisor

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Metal-Incorporated Mesoporous Silicates for Enhanced Olefin Metathesis for Propylene Production

Abstract

Synthesis of propylene from ethylene and 2-butene via Olefin Metathesis is an attractive and atom economical technology to augment the increasing propylene demand. The key hindrance in its commercial exploitation is the development of catalytic systems that selectively maximizes the propylene yield under milder reaction conditions. Silica-supported tungsten catalysts are used commercially to produce propylene; however, their activity is often limited due to low dispersion of the active W species resulting in olefin isomerization and cracking as side reactions. Hence, fundamental research is needed to develop metathesis catalysts with improved performance.

Several studies on catalyst synthesis clearly suggest that the dispersion and the nature of the metal oxide (MO_x, M = W, or Mo) species on the catalyst dictate the metathesis activity. In this work, we demonstrate that the metathesis activity of Mo-based catalysts can be enhanced by using catalysis synthesis techniques that enhance the dispersion of active Mo species. We developed a sol-gel method using TUD-1 as a support to synthesize new supported Mo catalyst formulations (Mo-TUD-1). The maximum propylene yield (~57%) observed with Mo-TUD-1 catalysts was superior when compared to conventional Mo/SiO_2 (propylene yield ~30%) at identical reaction conditions. *In situ* Diffuse Reflectance UV-Vis, Raman, Extended X-ray absorption fine structure (EXAFS), and *in situ* Pyridine-Fourier Transformed Infrared Spectroscopy (Py-FTIR) characterization experiments revealed that the population of isolated dioxo species, the active site precursors, were enhanced. This was accompanied by an increase in the Lewis acidity of the catalyst samples and increased propylene production. However, the catalysts deactivate with time suggesting that Mo oxide species with Brønsted acidity still form on the catalyst. To further increase the population of active sites that favor metathesis, we doped the Mo-based catalysts with small amounts of Lewis acid transition metals (M =Nb, Ta, Zr, Hf), based on our previous work with W-based catalysts. (continued on back)

(Abstract Continued)

All the doped catalyst performed better than the monometallic Mo catalyst, but the Mo doped with Nb ($Mo_2/Nb_{1.5}$-KIT-6)) showed propylene formation rates (54.2 ± 0.5 mmol $(mol_{Mo}\ s)^{-1}$) that are two-fold greater when compared to monometallic Mo_2/KIT-6 (28.7 ± 1.1 mmol $(mol_{Mo}\ s)^{-1}$) catalysts under identical reaction conditions (450 °C, 1 atm, WHSV = 4-18.2 mol/(mol_{Mo}·s), n(ethylene)/n(2-butene)/Argon in feed = 3/1/4 molar ratio, $X_{2\text{-butene}} < 10\%$) indicating that the dopant metals from group IV and V promotes metathesis activity. Diffuse reflectance UV-Vis, *R*aman, X-ray photoelectron spectroscopy (XPS), Extended X-ray absorption fine structure (EXAFS), and X-ray absorption near edge structure (XANES) characterizations show that compared to other bimetallic catalysts, MoNb catalysts displayed a high ratio of tetrahedral to octahedral MoO_x species suggesting an increase in the population of the isolated active site precursors. Moreover, pyridine adsorption enthalpies ($\Delta H_{ads,pyridine}$) as determined from the *in situ* TPD Py-FTIR experiments indicate that the interaction of pyridine with the isolated Nb^V is the strongest among the M sites with their strengths decreasing in the order (Nb>Ta>Zr>Hf). These results suggest that the addition of Nb (and the other transition metals) alters Mo coordination yielding additional bimetallic single site precursors ($MoNbO_x$) that are more active than their monometallic (Mo-O-Si) counterparts. This is further supported by a strong correlation between the propylene formation rates and ($\Delta H_{ads,pyridine}$) suggesting that the strength of the Lewis acid sites likely aids in better stabilization of the adsorbed olefins. A similar linear correlation was also observed between the isotropic chemical shifts of the adsorbed ^{15}N pyridine and the Lewis acid strengths ($\Delta H_{ads,pyridine}$) providing insights into the molecular origin of the electronic effects in the reactivity of olefin metathesis.

The selective enhancement of metathesis activity of Mo-based catalysts upon addition of a second metal such as Nb or Ta is a significant result and similar to those observed on W-based bimetallic catalysts system. It introduces a relatively simple technique for creating more active bimetallic single sites and tuning catalyst activity, most likely by varying the O=M=O bond angle with the added metal. The results are thus of fundamental significance in understanding the role of the dopant metal on the reaction mechanism and provide testable data for DFT predictions in determining the local structure of the active metal site for optimizing the metal reactant binding energies.