

# New Structural and Electronic Insights on Supported $(VO_x)_m/(M_1O_y)_n/(M_2O_z)_{bulk}$ Catalysts for the Oxidative Dehydrogenation (ODH) of Light Hydrocarbons

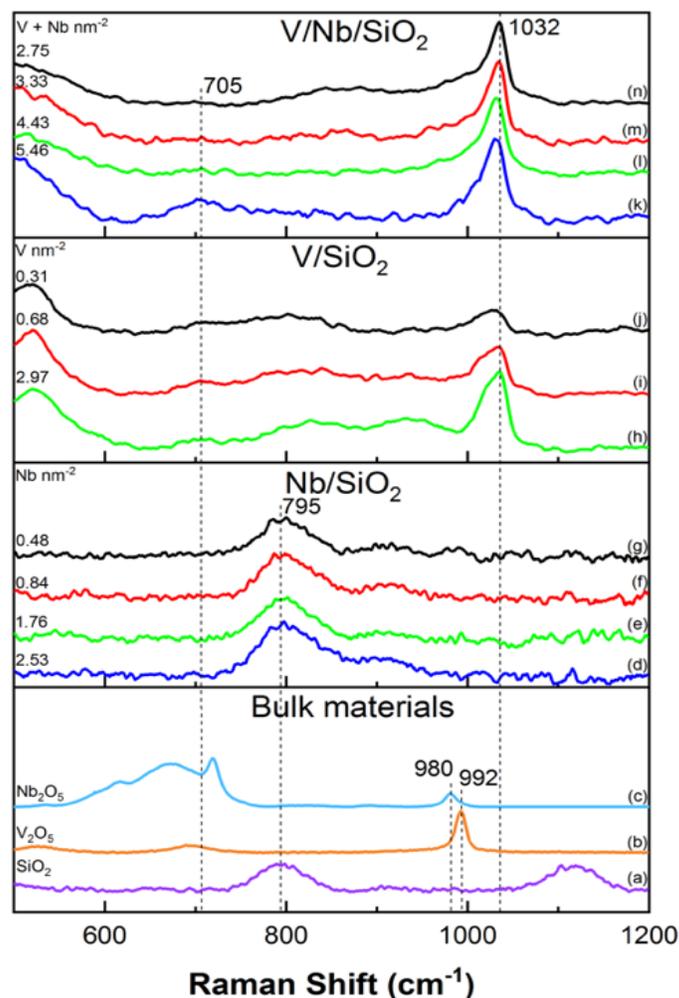
Kaitlyn Lawrence, Natalie Stephens, Jorge Moncada, Raj Thakur, Carlos A. Carrero

A heightened demand for commodity chemicals such as propylene and butylene paired with recent advances in hydraulic fracturing has motivated industry to turn to a domestic production feedstock: shale gas. Traditionally, C<sub>3</sub>-C<sub>4</sub> olefins were produced as byproducts using steam cracking of naphtha, an expensive, energy-intensive route. Therefore, as demand for olefins continues to soar, researchers have investigated other pathways of on-purpose production of C<sub>3</sub>-C<sub>4</sub> olefins.

One pathway that has been extensively studied in recent years is catalytic oxidative dehydrogenation, or ODH. The reaction is proven to run with relatively high yields of desired product even with relatively low energy inputs. Group V metals perform well in ODH due to their unique chemical nature, and supported vanadium oxide catalysts have proven a viable option of the Group V metals due to their low cost and high performance. [1] It has been found that synergistic effects in supported multi-component metal oxides enhance olefin productivity in ODH of light hydrocarbons [2,3]. The goal of this project was to synthesize a library of ternary supported metal oxide catalysts, all of which utilize vanadium as a main component  $(VO_x)_m-(M_2O_y)_n/(M_3O_z)_{bulk}$ , while varying the M<sub>2</sub> and M<sub>3</sub> metals (Si, Ti, Zr, Al, Ce, Nb). Supported catalysts utilize an inert support material to which the catalytic active sites are anchored, whereas bulk catalysts are composed of a uniform catalyst through the solid particle. Support is often used to lower the cost of catalysts while maintaining a high number of active sites.

In this project, the ratio of V:M<sub>2</sub> metals was tuned with the goal of achieving monolayer coverage, a term used to describe the two-dimensional dispersion of MO<sub>x</sub> active sites on the outer layer of the support. These samples were characterized by Brunauer-Emmett-Teller surface area tests (BET), inductively coupled plasma atomic emission spectroscopy (ICP-AES), Raman spectroscopy (Figure 1), and H<sub>2</sub>-TPR (Figure 2).

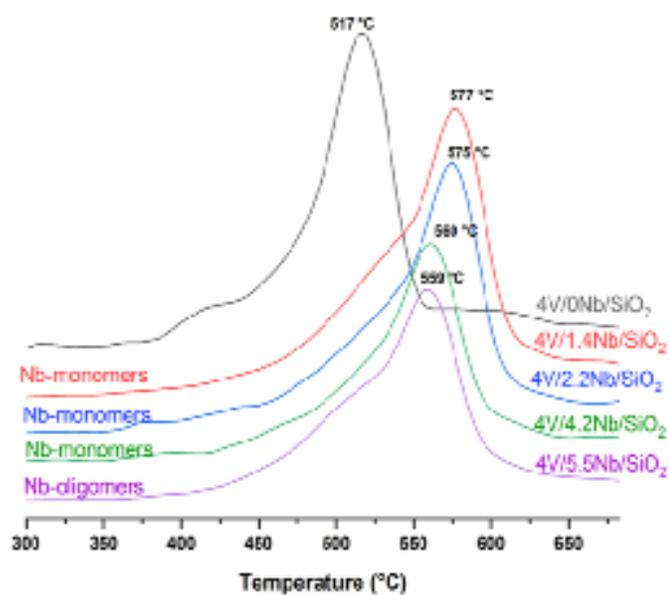
The catalysts were then tested catalytically in a custom reactor set up. We performed the oxidative dehydrogenation of isobutane to produce isobutylene (Figure 3).



**Figure 1:** *In situ* Raman spectra for bulk, supported binary and ternary metal oxides. Metal coverage obtained from BET and ICP is labeled along its correspondent Raman spectra.

The final goal was to establish structure-reactivity relationships for the design of more selective, stable and active catalysts for future ODH experiments. The catalytic activity of supported binary  $(M_2O_y)_n/(M_1O_x)_{bulk}$  and ternary  $(M_3O_z)_m-(M_2O_y)_n/(M_1O_x)_{bulk}$  metal oxide catalysts essentially depends on the presence of two-and

three-dimensional M<sub>2</sub>O<sub>y</sub> and M<sub>3</sub>O<sub>z</sub> species, the M<sub>3</sub>:M<sub>2</sub> ratio (coverage of each component), and their spatial relation. We found that the extent of synergistic effects strongly depends on these same factors. Our study shows that the extent of synergistic effects is greater on reduced metal oxides. This is because we cannot reduce all V<sup>5+</sup> and Nb<sup>5+</sup> sites to V<sup>3+</sup> and Nb<sup>3+</sup> under our reaction conditions and therefore, metal cations (V<sup>5+</sup>, V<sup>4+</sup>, V<sup>3+</sup>, Nb<sup>5+</sup>, Nb<sup>4+</sup>, Nb<sup>3+</sup>) at different amounts and oxidation states are present on the catalyst's surface. The formation of these Mn<sup>+</sup> species depends on both the reaction conditions (e.g., temperature, residence time) and the reducing agent (e.g., hydrogen, hydrocarbon).

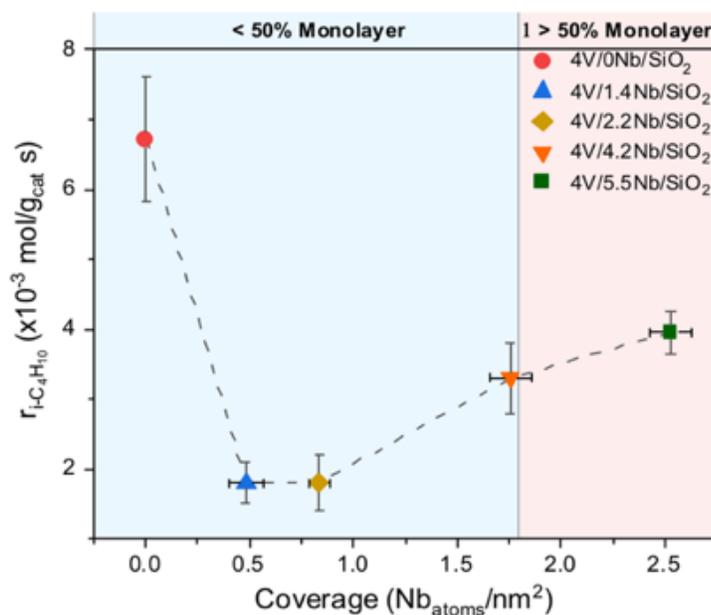


**Figure 2:** H<sub>2</sub>TPR profiles for VNb/SiO<sub>2</sub> catalysts. Explicit indication for samples containing Nb monomers and oligomers are shown on the left side of each curve.

### Statement of Research Advisor:

Kaitlyn has been learning and developing new strategies to prepare supported metal oxide catalysts for the upgrading of natural gas. During the last year, Kaitlyn has determined the most important variables to control and tune the desired molecular species needed to perform specific catalytic reactions. Currently, we are both compiling these important results in a peer-reviewed journal (ChemCatChem) and using them to continue our research in selective oxidation catalysis for light hydrocarbons.

—Carlos A. Carrero, Chemical Engineering



**Figure 3:** Isobutane consumption rate as a function of Nb coverage at 420 °C. Catalyst mass: 30-40 mg. Total flow: 60 sccm.

### References:

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2. C. A. Carrero, S. P. Burt, F. Huang, J. M. Venegas, A. M. Love, P. Mueller, H. Zhu, J. T. Grant, R. Mathison, M. P. Hanrahan, A. Rossini, M. Ball, J. Dumesic and I. Hermans, "Supported two- and three-dimensional vanadium oxide species on the surface of  $\beta$ -SiC," *Catalysis Science & Technology*, pp. 3707-3714, 2017.
3. J. T. Grant, A. M. Love, C. A. Carrero, F. Huang, J. Panger, R. Verel and I. Hermans, "Improved Supported Metal Oxides for the Oxidative Dehydrogenation of Propane," *Topics in Catalysis*, pp. 1545-1553, 2016.