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Project Title: Catalysts for Direct Conversion of Methane

Principal Investigator: George W. Huber, Harvey D. Spangler Professor in the Chemical and Biological Engineering at the University of Wisconsin - Madison

Co-Principal Investigators: None

Recent and Ongoing Work

During the previous year, we have completed the design and construction of a continuous flow reactor, shown in Figure 1, capable of performing steady-state isotopic kinetic analysis (SSITKA). SSITKA is an advanced catalyst characterization technique that allows for quantification of the number of surface intermediates and the effective surface residence time of a catalytic system. This analysis is performed by using a high-speed switching valve to induce a carefully controlled switch between a reactant and its isotopically labeled analog without disturbing the reaction and then analyzing the concentration of labeled reaction products as a function of time via an online mass spectrometer. Quantification of the characteristics of the catalyst surface is possible by monitoring the amount of time it takes for the isotopically labeled reactant to pass through the catalytic system. In this way, the SSITKA system allows us to count active catalytic sites on systems that have remained challenging to characterize with traditional chemisorption or titration methods.

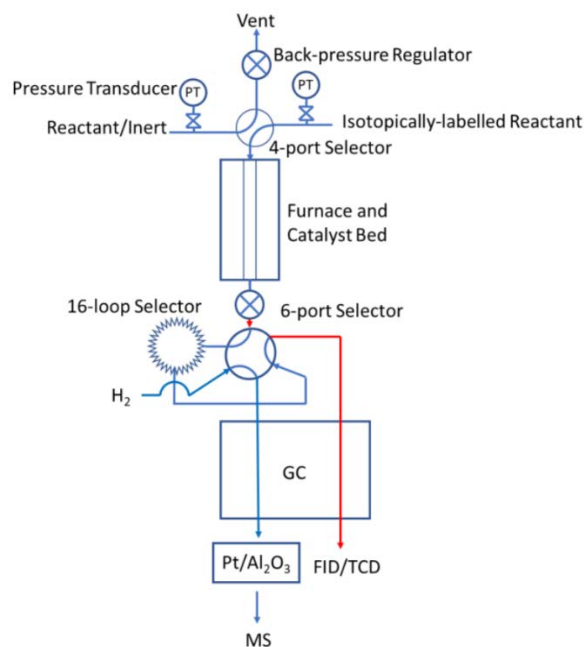


Figure 1: Reactor system for multi-product SSITKA. Design based on work by Goodwin et al^[1] and Davis et al^{[2]-[3]}.

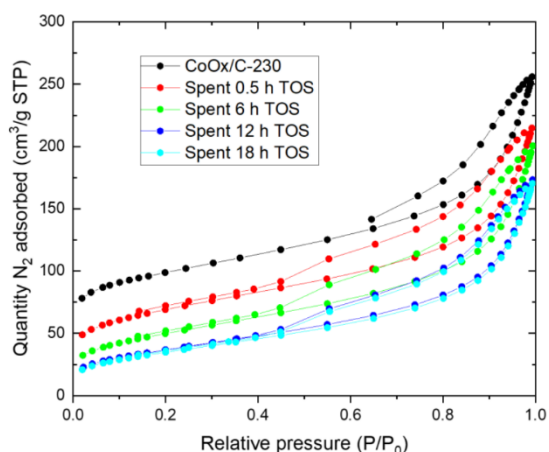


Figure 2: N₂ adsorption isotherms of fresh and spent CoO_x/C at various TOS for ethylene oligomerization.

of rapid catalyst deactivation. However, after this initial period, deactivation slowed down to a pseudo steady-state condition that was stable enough to complete the analysis.

We have started implementing the use of this reactor to measure the intrinsic activity and dispersion of CoO_x/C active sites in the oligomerization of ethylene. These carbon-supported cobalt oxide catalysts have been demonstrated to be one of the most selective heterogeneous materials to produce n-octenes^[4] and have been shown to produce similar linear distributions for ethylene and 1-butene oligomerization^[5]. In order to perform the SSITKA studies, the catalyst needs to achieve steady-state conditions, which was difficult for CoO_x/C given the rapid deactivation observed during the first few hours on stream. Using N₂ adsorption techniques, we determined that, as shown in Figure 2, pore filling, or a continuous decrease in surface area, was the main source

Therefore, we performed SSITKA of ^{13}C -labeled C_2H_4 to count active oligomerization sites in order to extract reliable estimates of both dispersion and kinetic parameters for CoO_x/C . The normalized transient response for CoO_x/C is shown in Figure 3. The inert tracer and $^{12}\text{C}_2\text{H}_4$ dropped off rapidly while the $^{12}\text{C}_4\text{H}_8$ and $^{12}\text{C}_6\text{H}_{12}$ species had much longer transient times, consistent with a stronger binding strength for longer alkyl intermediates. We determined that the average surface residence times for $^{12}\text{C}_2\text{H}_4$ and $^{12}\text{C}_4\text{H}_8$ were 2.7 and 29 s, respectively, which corresponded to a cobalt dispersion of 3.2%. The surface of CoO_x/C was found to be covered primarily with ethylene, which rapidly desorbed upon the isotopic switch. By counting the active surface sites, we calculated that after 5 h time on stream, < 0.2% of cobalt was active for oligomerization with an average turnover frequency (TOF) of 0.4 s^{-1} under our reaction conditions and after 5h time-on-stream.^[6]

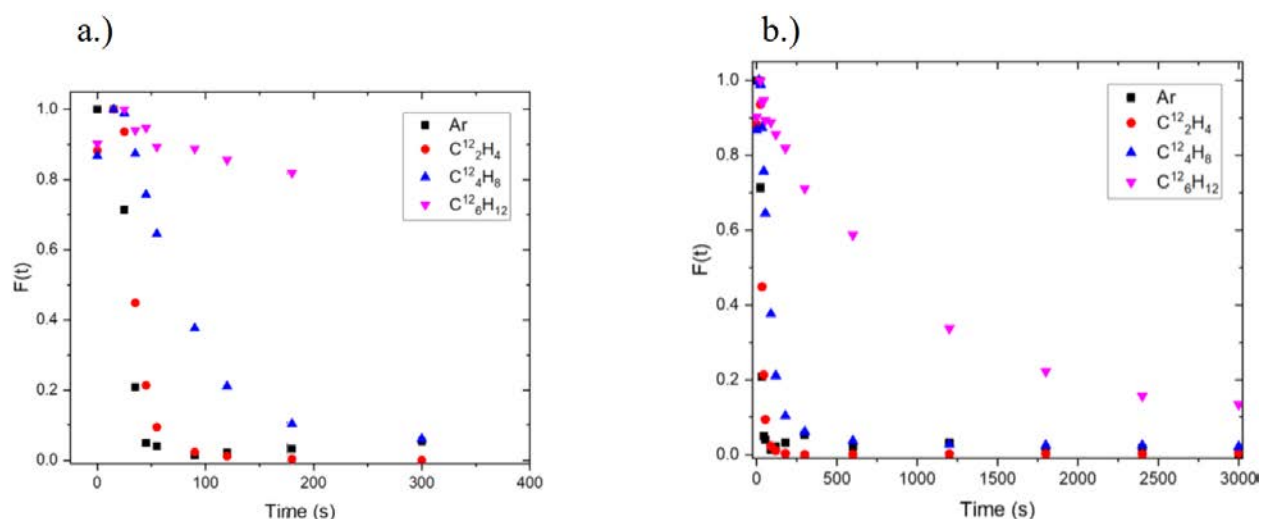


Figure 3: Normalized transient response for multi-product SSITKA of C_2H_4 oligomerization. a) Data zoomed in b) Entire data range.

Future Work

Besides the use of SSITKA for the characterization of the CoO_x/C catalysts previously discussed, we are currently working towards the implementation of this technique to analyze additional catalytic systems, including a Pd/C catalyst for formic acid decomposition. Our plan is to combine ongoing efforts in reactivity studies and microkinetic modeling with SSITKA experiments in order to elucidate the catalytic surface of the Pd system and validate the computational models.

Impact on Student Researchers

Over the last year, this research grant funded graduate student Keishla Rivera-Dones and recent graduate Dr. Joseph Chada. These researchers have continued to develop and apply skills in catalyst synthesis and characterization as well as reactor and analytical system design and construction. They have also assisted in developing manuscripts.

References

- ^[1] Shannon, S.L.; Goodwin, J.G., *Chem. Rev.* **1995**, 95, 677-695. ^[2] Hanspal, S.; Young, Z.D.; Shou, H.; Davis, R.J. *ACS Catal.* **2015**, 5, 1737-1746. ^[3] Shou, H.; Davis, R.J. *J. Catal.* **2013**, 306, 91-99. ^[4] Xu, Z.; Chada, J.P.; Zhao, D.; Carrero, C.A.; Kim, Y.T.; Rosenfeld, D.C.; Rogers, J.L.; Rozeveld, S.J.; Hermans, I.; Huber, G.W. *ACS Catal.* **2016**, 6, 3815-3825. ^[5] Xu, Z.; Chada, J.P.; Rosenfeld, D.C.; Rogers, J.L.; Hermans, I.; Huber, G.W. *J. Catal.* **2017**, 354, 213-222. ^[6] Chada, J.P.; Jonathan, A.; Konz, Z.M.; Maccoux, B.D.; Xu, Z.; Zhao, D.; Hermans, I.; Dumesic, J.A.; Huber, G.W. *in-preparation*.