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Project Title: Catalysts for Direct Conversion of Methane

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Co-Principal Investigators: None

Recent and Ongoing Work

During the previous year, we have used the steady-state isotopic kinetic analysis (SSITKA) technique to better understand the interactions between reactive intermediates and the catalyst surface during acetone hydrogenation to isopropanol over supported platinum catalysts. 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 using a system like that described in Figure 1, where a high-speed switching valve is used to induce a carefully controlled switch between a reactant and its isotopically labeled analog without disturbing the reaction. The concentration of labeled reaction products is then analyzed as a function of time via an online mass spectrometer.

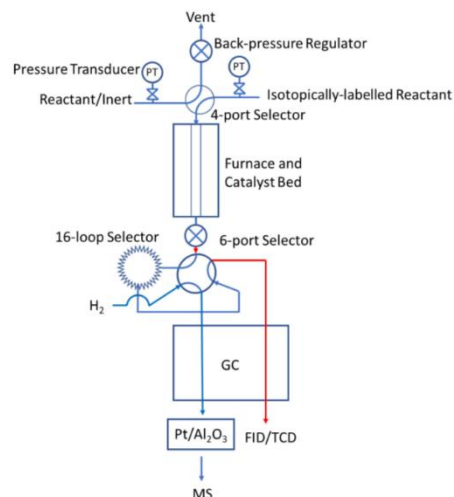
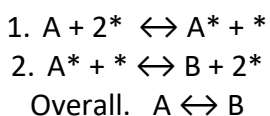


Figure 1: Reactor system for multi-product SSITKA. Design based on work by Goodwin^[1] and Davis^{[2]-[3]} et al.

A microkinetic model for acetone hydrogenation over platinum

was developed to describe experimental steady-state reactivity data at 353 K by combining DFT-derived thermodynamic properties and surface energetics with a detailed 10-step reaction mechanism. In order to apply this model to transient reactivity, the favored steady-state 5-step pathway was condensed into the generalized 2-step system shown in Scheme 1. This model has been used to predict the transient behavior of the acetone hydrogenation reaction over platinum following desorption (complete removal of acetone from feed) and SSITKA (isotopic substitution of acetone in the feed) profiles. The model for a desorption case predicts transients in the order of seconds for the acetone and isopropanol species and shows minimal delay between removal of the argon tracer and complete acetone elution, suggesting negligible interaction between acetone and the catalyst surface. Furthermore, the surface coverage by the most abundant reactive intermediate (MARI) changes minimally during a transient induced by



Scheme 1: Generalized 2-step scheme for a hydrogenation reaction

removal of the reactant acetone species. This behavior suggests that coverage effects (for which the interaction of the MARI with the surface becomes stronger at low surface coverages) suppress the ability to decrease the presence of the MARI species solely by desorption. On the other hand, the normalized transient flow rates predicted by the SSITKA model show a considerably longer transient for the isopropanol product than that predicted by the desorption model. More importantly, the SSITKA model predicts complete removal of the MARI species upon substitution of the reactant feed.^[4]

The existence of coverage effects was probed experimentally by inducing desorption and reactive transients over supported platinum catalysts using the apparatus shown in Figure 1. The desorption transient was induced by abruptly removing the acetone from the feed while maintaining a constant overall flowrate, whereas the SSITKA transient was induced by substituting acetone with the structurally similar ketone, pentanone. Figure 2 shows the transient profiles for both cases and it can be easily seen that a longer decay time exists for the isopropanol species during a SSITKA transient when compared to

desorption. The quantification of surface residence times and active site counts were evaluated as a function of total flow rates for both transient scenarios to test for the presence of re-adsorption effects.^[4]

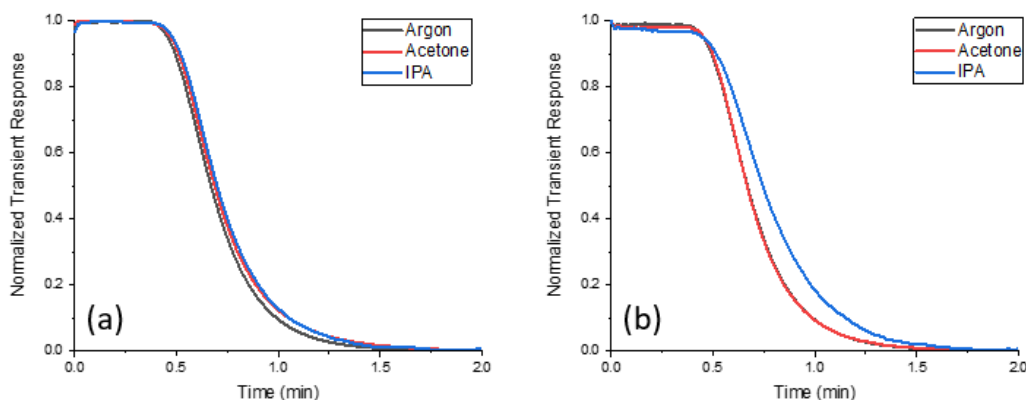


Figure 2: Response profiles during (a) desorption and (b) SSITKA transients for acetone hydrogenation over a Pt/ α -Al₂O₃ catalyst

The intrinsic time constants and site densities for each case can be determined by extrapolating to infinitely fast flowrates. The results in Table 1 show that while the time constants are fairly similar for both transients, the active site count is approximately 4 times larger during a SSITKA response when compared to desorption. This difference in site density confirms that a significant amount of adsorbed intermediates remains on the catalyst surface following removal of the acetone feed, and those intermediates can only be removed by introducing an alternative reactant species to displace them from the platinum surface. Moreover, the intrinsic site density obtained for the reactive transient is in agreement with the active site density determined via CO chemisorption, thus providing experimental evidence for complete removal of the MARI species from the catalytic surface, as was originally predicted by the theoretical models.^[4]

Table 1: Intrinsic kinetic parameters from desorption and SSITKA transient profiles

Experiment	Intrinsic Time Constant (sec)	Intrinsic Site Density ($\mu\text{mol}/\text{g}_{\text{cat}}$)
Desorption	1.8	2.6
SSITKA	2.2	10.7

Future Work

Besides the use of SSITKA for the characterization of the Pt-based catalysts previously discussed, we are currently using this technique to study Pd-based catalysts for ethylene hydrogenation and working towards the implementation of this technique for etherification reactions. 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, who has 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] Rivera-Dones, K.R.; Huber, G.W.; Dumesic, J.A. *Manuscript under Development*