

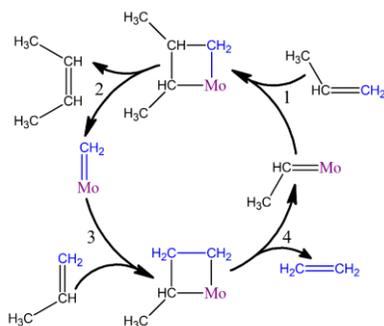
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## In Situ and Operando Spectrokinetic Studies of Tungsten Based Catalysts for Olefin Metathesis

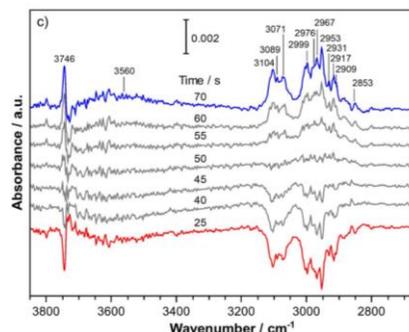
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### Project Objectives

This research seeks to understand the nature of active sites and intermediate species during catalyzed olefin metathesis. The main objectives include the use of in situ/operando FTIR, Raman, and UV-vis spectroscopies with kinetics to determine reaction intermediates and active sites in SiO<sub>2</sub> and TiO<sub>2</sub>/SiO<sub>2</sub> supported WO<sub>x</sub> catalysts for olefin metathesis. Propylene metathesis to ethylene and 2-butene (and reverse reaction to produce propylene) is shown in **Scheme 1** and used as the test reaction.



**Scheme 1.** Chauvin's mechanism for propylene (or ethylene and 2-butene: reverse cycle) metathesis.

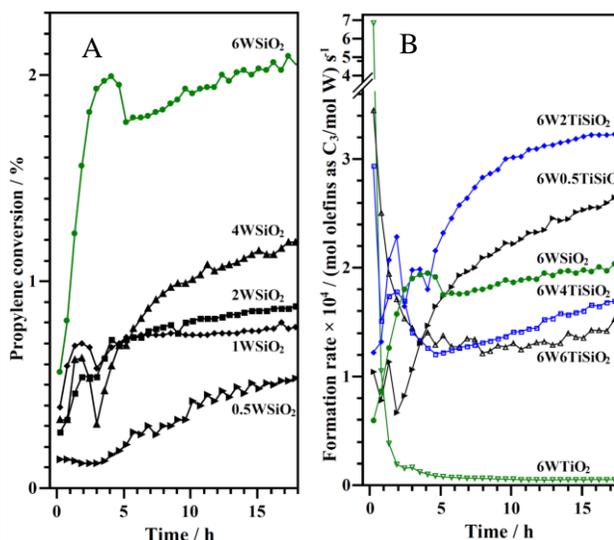


**Figure 1.** Propylene metathesis ME-DRIFTS on Mo-TUD-1 during water modulation (0-0.25%) at 450 °C, 101 kPa.

### Research Progress and Impact of Research

We developed a low void-volume in situ diffuse reflectance reaction cell for the study of catalyzed gas phase reactions that allowed rapid exchange of gases with a residence time of ~1 s at gas flow rates of ~45 cm<sup>3</sup>/min [1]. These conditions enabled the implementation of modulation excitation (ME) + DRIFTS and DR-UV-vis spectroscopies [1]. These techniques were applied to propylene metathesis on a Mo(4.4 wt%)-TUD-1 catalyst at reaction conditions (450 °C, 101 kPa, ~65 mg catalyst). ME-DRIFTS during water (0~0.25%) modulation (1/90 Hz) (**Figure 1**) evidenced the presence of adsorbed ethylene (3108 cm<sup>-1</sup>) and propylene (3091 cm<sup>-1</sup>) and metal carbenes (**Scheme 1**) [2]: 1) Mo(VI)-methylidene (3071 and 2953 cm<sup>-1</sup>); 2) Mo(VI)-ethylidene (2999, 2931, 2909, and 2853 cm<sup>-1</sup>); and 3) Mo(VI)-cyclobutane square pyramidal structures (2999, 2967, and 2917 cm<sup>-1</sup>). Additionally, ME-DR-UV-vis during propylene modulation (not shown) evidenced Mo<sup>6+</sup> reduction at higher concentrations of propylene. These results offer support for formation of metal carbenes likely via a pseudo-wittig mechanism with partial reduction of Mo<sup>6+</sup> to Mo<sup>4+</sup> [3].

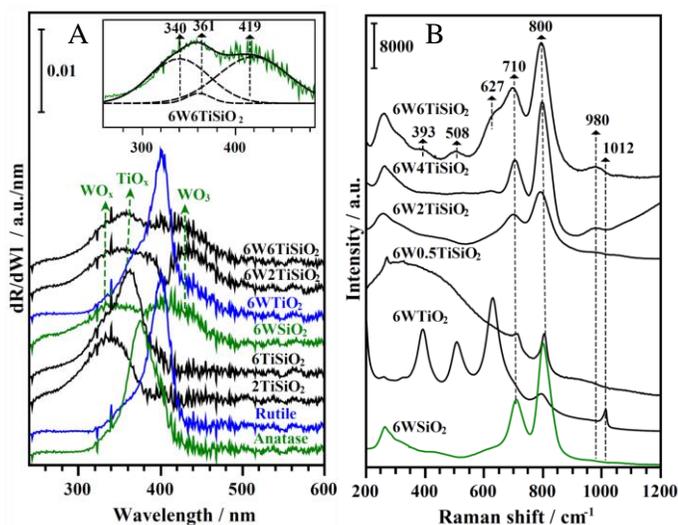
SiO<sub>2</sub> (~50 m<sup>2</sup>/g), TiO<sub>2</sub>(y = 0.5-6 wt% prepared by IWI)-SiO<sub>2</sub>, and TiO<sub>2</sub> (anatase, ~50 m<sup>2</sup>/g) supported (x = 0.5-6 W/nm<sup>2</sup>) WO<sub>x</sub> catalysts (labeled as xWyTiSiO<sub>2</sub>) were prepared by incipient wetness impregnation (IWI) using titanium isopropoxide and ammonium metatungstate as the Ti and W precursors, respectively. It has been recognized that highly dispersed dioxo WO<sub>x</sub> species are active for olefin metathesis, but that on SiO<sub>2</sub> support only low W contents (monolayer coverage at <1 W/nm<sup>2</sup>) allow a high density of such species [4,5]. Since WO<sub>x</sub> monolayer coverage on TiO<sub>2</sub> can be achieved at relatively higher W contents (<4.5 W/nm<sup>2</sup>), it was hypothesized that yTiSiO<sub>2</sub> supports would favor WO<sub>x</sub> dispersion and thus resulting in higher activity towards olefin metathesis. During propylene metathesis at 450 °C, as expected, propylene conversion on xWSiO<sub>2</sub> catalysts increased with WO<sub>x</sub> content (up to 6 W/nm<sup>2</sup>) because of the higher WO<sub>x</sub> amount (not density) of dispersed WO<sub>x</sub> species (**Figure 2A**). However, at such high W loadings (higher than monolayer coverage), lower WO<sub>x</sub> dispersion was expected because of formation of WO<sub>3</sub> nanoparticles. Thus, the 6WSiO<sub>2</sub> catalyst was selected as an active but poorly WO<sub>x</sub> dispersed catalyst to study its modification by addition of TiO<sub>x</sub> domains to the SiO<sub>2</sub> support.



**Figure 2.** Propylene metathesis (450 °C, 101 kPa propylene) on SiO<sub>2</sub>, TiO<sub>2</sub>-SiO<sub>2</sub>, and TiO<sub>2</sub> supported WO<sub>x</sub> catalysts.

**Figure 2B** shows the olefins temporal (e.g., ethylene, butenes, hexenes) formation rate normalized to propylene on  $xW_yTiSiO_2$  catalysts. Several observations can be made: 1)  $6WTiO_2$  initial activity was significantly higher than the corresponding  $6WSiO_2$ , but the catalyst deactivated quite rapidly due to coke deposition as monitored by in situ Raman (not shown) at similar reaction conditions. This result is quite unusual, and it is possible that highly dispersed mono-oxo  $WO_x$  species present on  $TiO_2$  (absence of  $WO_3$  signals from XRD, not shown, and Raman signal at  $1012\text{ cm}^{-1}$ ) [4], unlike dioxo  $WO_x$  species on  $SiO_2$  catalysts [6], are also active for olefin metathesis possibly via mono-oxo  $\leftrightarrow$  dioxo conversion at high temperatures [5]. 2)  $6WSiO_2$  activity increased with time possibly due to slow formation of surface intermediates. 3) High  $TiO_x$  content ( $6W6TiSiO_2$ ,  $6W4TiSiO_2$ ) catalysts resembled the  $6WTiO_2$  catalyst trends, whereas lower  $TiO_x$  contents ( $6W2TiSiO_2$ ,  $6W0.5TiSiO_2$ ) resembled the  $6WSiO_2$  catalyst behavior. The quasi-steady state activity of the  $6W2TiSiO_2$  and  $6W0.5TiSiO_2$  was, however, higher than that for the unmodified  $6WSiO_2$  catalyst, suggesting the validity for the proposed hypothesis that  $TiO_x$  domains increase  $WO_x$  dispersion.

Differential DR-UV-vis and in situ Raman show the presence of features characteristic of polymeric  $WO_x$  (UV-vis:  $340\text{ nm}$ ; Raman:  $980\text{ cm}^{-1}$ ) and  $TiO_x$  (UV-vis:  $361\text{ nm}$ ; Raman:  $393$ ,  $508$ , and  $627\text{ cm}^{-1}$ ) and  $WO_3$  nanoparticles (UV-vis:  $419\text{ nm}$ ; Raman:  $710$  and  $800\text{ cm}^{-1}$ ) [4] in  $xW_yTiSiO_2$  (**Figure 3A and 3B**). In particular, Raman spectroscopy evidences the presence of highly dispersed  $TiO_x$  domains and dio-oxo  $WO_x$  species in the  $xW_yTiSiO_2$  catalysts with respect to  $xWSiO_2$ . These results suggest that highly dispersed  $TiO_x$  domains (such as those in  $6W2TiSiO_2$ ) probably adsorb W precursors that later convert into highly dispersed, active and stable dioxo  $WO_x$  species. Overall, these results show that  $xWSiO_2$  modification by addition of secondary metal oxides (e.g.,  $TiO_2$ ) appears to be a simple and useful strategy to improve metathesis catalysts likely via increased  $WO_x$  dispersion. Additional in situ characterization of intermediates species, active sites, and acidity are under way to further understand their nature to help develop improved and novel olefin metathesis catalysts.



**Figure 3.** A) Ex situ DDR-UV-vis (BaSO<sub>4</sub> reference) and B) in situ Raman at  $450\text{ }^\circ\text{C}$  in  $O_2(20\%)/Ar$  before metathesis reaction.

### Impact on Career and Participating Students

A Ph.D. student is funded through this award. She has helped advance the development of a new in situ reaction cell, the application of novel in situ modulation excitation spectroscopic techniques for detection of surface intermediates and for the study of olefin metathesis catalysts. Such research will place her in leading roles to further apply such techniques to understand catalytic cycles and to develop improved and novel catalysts. Two chemical engineering undergraduate students also participated in our research efforts for testing and characterizing catalysts. Under the PI and graduate student guidance, they mastered catalysts reactivity and spectroscopic characterization techniques and provided them with valuable hands-on lab experience to carry over their professional careers. The ACS-PRF funding has allowed the PI to establish and further develop leading and novel in situ/operando techniques while exploring new applications of relevance to catalysis. As a result, the PI recently received the NSF-CAREER award (2019-2024) to gain insights into reaction intermediates, charge transfer kinetics, and metal-support interactions in vapor phase alcohol oxidation reactions catalyzed by supported gold nanoparticles. Additional products of the research include two published manuscripts describing the design, modelling, and application of the new in situ cell [1], while two more are in preparation to report the findings briefly described above.

### References

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