

2/18/20

Overall status: **On track****Overview of the project**

This ACS/PRF project aims to the development of fundamental understanding on the reactivity of sulfated metal oxides as well as mixed metal oxides on the phenol alkylation reaction where tertiary butyl alcohol is used as the alkylating agent. At the core of our research, understanding i) the kinetics of the phenol alkylation over various catalysts as well as ii) the evolution of active sites (i.e. sulfated species) by means of in-situ vibrational spectroscopy comprise the major directions. The overall status of the project is on track and several milestones that have been reached are highlighted next.

**Project milestones**

- **Synthesis of sulfated metal oxides and mixed metal oxides based on  $\text{SnO}_2$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$ .**
  - A series of catalysts have been prepared using well-reported in the open literature methods based on sol-gel or co-precipitation techniques. Specifically, we have synthesized the following catalysts:  $\text{SO}_4^{2-}/\text{SnO}_2$ ,  $\text{SO}_4^{2-}/\text{ZrO}_2$ ,  $\text{SO}_4^{2-}/\text{TiO}_2$ ,  $\text{SO}_4^{2-}/(1)\text{SnO}_2 - (10)\text{ZrO}_2$ ,  $\text{SO}_4^{2-}/(1)\text{SnO}_2 - (1)\text{ZrO}_2$  and  $\text{SO}_4^{2-}/(10)\text{SnO}_2 - (1)\text{ZrO}_2$ . Efforts during the next reporting period will be placed on synthesizing sulfated  $\text{ZrO}_2$ - $\text{TiO}_2$  and  $\text{SnO}_2$ - $\text{TiO}_2$  mixed metal oxides to complete all the possible combinations initially planned.
- **Characterization of catalysts via vibrational spectroscopy, X-Ray Diffraction and acidity measurements**
  - At first, the mixed metal oxides have been studied by means of XRD to unravel possible crystalline changes under calcination. The effect of the ratio of metal oxide precursors was evaluated. In addition, the effect of calcination temperature on the crystallinity of the synthesized mixed phase was also evaluated. Relevant results are shown in Figure 1.

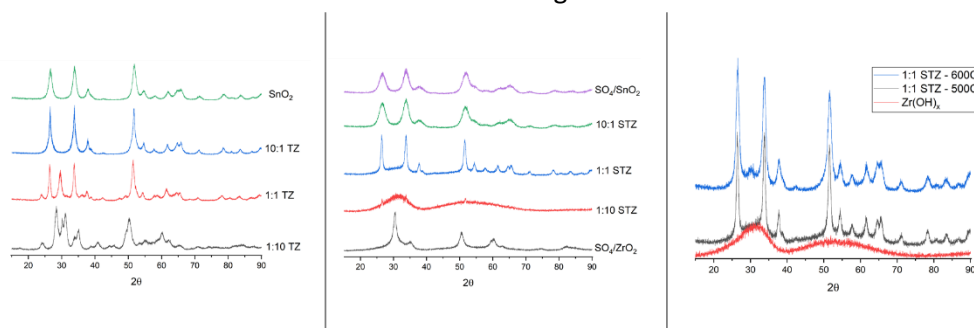


Figure 1: XRD patterns of mixed Sn-Zr samples (non-sulfated and sulfated catalysts are shown for comparison)

- The synthesized materials, have been evaluated by means of in-situ Raman spectroscopy under hydrated (25°C) and dehydrated conditions in the temperature range of 100-500°C. The stability of sulfated species has been also evaluated. In Figure 2, we show representative results for three catalysts. It is evident that there is a

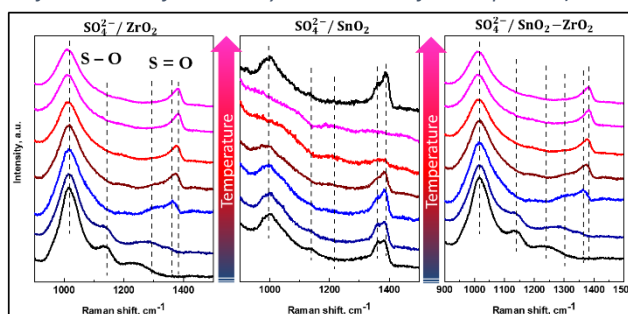


Figure 2: In-Situ Raman upon temperature increase to study active species evolution

clear evolution of the sulfated species upon increasing temperature that pertains to hydrated  $\rightarrow$  bidentate  $\rightarrow$  tridentate  $\text{SO}_4^{2-}$  transformation.

- **Catalytic evaluation | Phenol alkylation with tertiary butyl alcohol as alkylating agent**

- Sulfated metal oxides and mixed metal oxides have been catalytically evaluated in order to identify promising candidates for the phenol alkylation reaction. It is known that the presence of -OH groups in phenol, kinetically promotes the formation of the ortho-alkylated product even though steric hindrance has been highlighted as one drawback. In the presence of moderate acids, we expect that the para-alkylated product will be favored over the ortho-. To that end, a series of catalytic data have been collected under  $120^\circ\text{C}$  and same catalyst loading. Relevant results are shown in figure 3. Among the catalysts tested, Sulfated  $\text{SnO}_2$  as well as the commercial phenolic resin, Amberlyst 15, show very promising catalytic reactivity with high selectivity to the mono alkylated products. Since all the data presented in Figure 3 pertain to 4hr reaction time, we have evaluated kinetically the three more promising catalysts, i.e. S- $\text{SnO}_2$ , S- $\text{ZrO}_2$  and Amberlyst 15, and relevant results are presented in Figure 4. We observe that even at very early reaction time, the Amberlyst 15 and S- $\text{SnO}_2$  show enhanced reactivity as far as TBA conversion is concerned while S- $\text{ZrO}_2$  is not very active. Extrapolating at initial conditions, in all three cases we observe a conversion of around 35% which is close to the equilibrium conversion for the etherification reaction where phenol and TBA lead to tertiary butyl ether. Interestingly, we find that the pure  $\text{SnO}_2$  without any sulfated species, appears to be active. We hypothesize that the intrinsic acidity of surface Sn-OH groups are responsible of the enhanced activity. Although pure  $\text{TiO}_2$  is totally inactive and promotes only the formation of phenolic ether, future efforts will be placed on studying more pure acidic oxides on the phenol alkylation reaction.

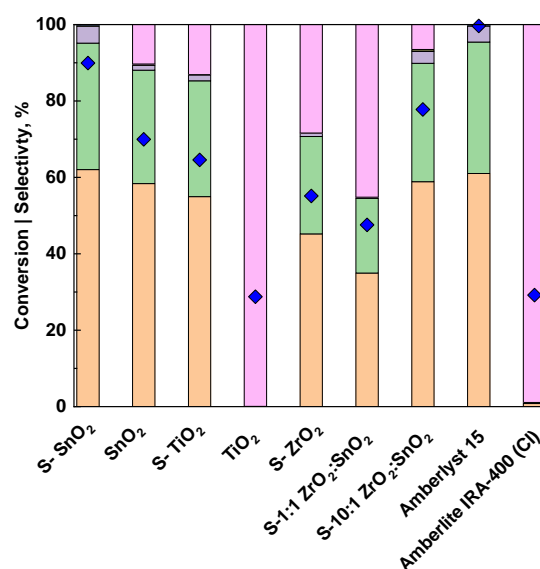


Figure 3: Catalytic performance of series of catalysts at  $120^\circ\text{C}$  and reaction time of 4hr

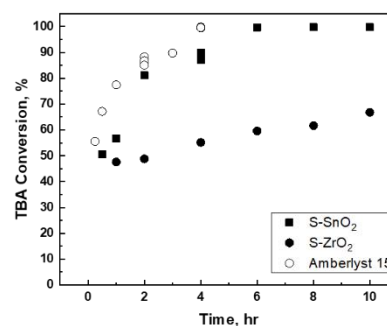


Figure 4: Kinetic data for three promising catalysts

### Project Outcomes

- This work has been presented in several local and national conferences including AIChE and New York Catalysis Society annual meetings
- Two manuscripts are in preparation regarding characterization and catalytic evaluation of the oxides studied and will be submitted by the end of June 2020
- A collaboration with a faculty member from CBE at Rutgers University (Prof. Haoran Zhang) has been established. In this project we aim to design processes where metabolic engineering is coupled with reactive desorption to targeted make alkylated phenolic compounds directly from biomass.