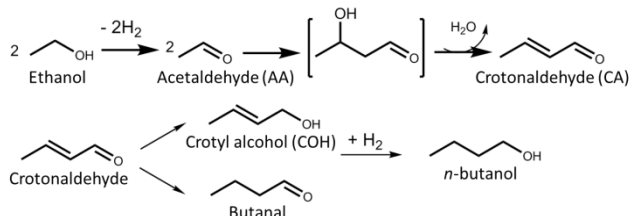


## Fundamental Insights into Heterogeneously Catalyzed Reactions using Modulation Excitation FT-IR and Raman Spectroscopy

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We constructed an *operando* modulation excitation spectroscopy diffuse reflectance infrared spectroscopy setup with an online mass spectrometer (MES-DRIFTS-MS) in first year grant period. By using MES techniques coupled with phase sensitive detection (PSD), the signal from active species is enhanced while the signal from spectator species is filtered out because spectator species do not respond to the modulation. In last annual report, we reported on the insights of ethanol coupling to 1,3-butadiene as a model reaction by observing the surface intermediates and demonstrating the advantages of using MES-DRIFTS-MS. In year two, we expanded the use of the MES-DRIFTS-MS technique to explore a second catalytic system: ethanol coupling to *n*-butanol over a hydroxyapatite (HAP) catalyst. HAP has been reported in the literature to be a very selective catalyst for this reaction. However, there is a lack of molecular understanding of the reaction mechanism, making it an ideal candidate for study using MES-DRIFTS-MS.

The energy density of *n*-butanol is higher than ethanol which makes the ethanol to *n*-butanol transformation highly attractive. Several catalyst systems have been studied for ethanol coupling to *n*-butanol such as MgO, Mg/Al mixed

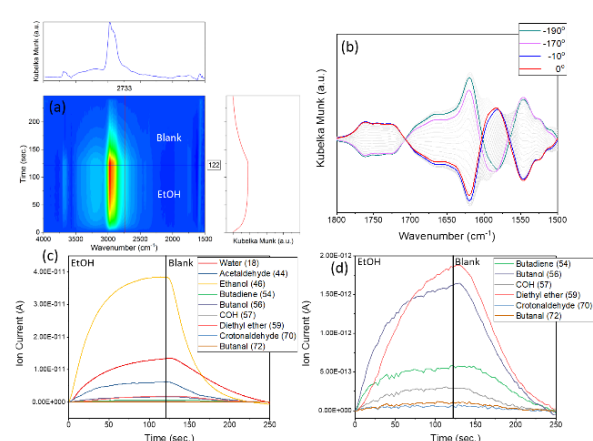


**Scheme 1.** Proposed reaction mechanism of ethanol coupling to *n*-butanol.

metal oxides, and HAP. HAP has been reported as one of the best catalysts with high *n*-butanol selectivity (~75%) at 10% conversion. Several reports claimed that the proper ratio of acidic to basic sites (columnar hydroxyl groups,  $\text{Ca}^{2+}$ , and  $\text{PO}_4^{3-}$ ) in HAP are responsible for its excellent performance in ethanol coupling. Although some

mechanistic studies have been reported based on kinetic analysis, direct observations via spectroscopic results are still needed as complimentary evidence to fully understand the reaction mechanism. To this aim, we have utilized MES-DRIFTS-MS as a technique to investigate ethanol coupling to *n*-butanol over HAP.

The well-accepted mechanism for ethanol coupling to *n*-butanol by HAP via the Guerbet pathway is shown in



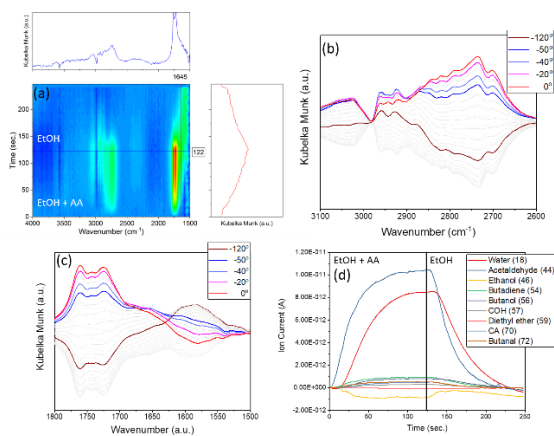
**Figure 1.** Modulation experiment between EtOH and argon flow over hydroxyapatite at 330°C. a) Time-domain, b) Phase-domain DRIFTS spectra, c,d) Recorded MS spectra.

Scheme 1. Ethanol is first dehydrogenated into acetaldehyde (AA) and then aldol condensation occurs between two units of AA to produce crotonaldehyde (CA). CA subsequently undergoes hydrogenation to crotyl alcohol (COH) or butanal and is then further hydrogenated to *n*-butanol. To elucidate the formation of the proposed species, the MES-DRIFTS-MS experiment is performed by first flowing ethanol with argon in the first half period and pure argon carrier gas in the second half period over a commercial hydroxyapatite sample at 330 °C. In the time domain spectra (Figure 1a), the appearance of signals at 2733 and 1758  $\text{cm}^{-1}$  with a 7 second time delay can

be attributed to the C-H stretching and C=O stretching from the AA intermediate. AA can also be observed in the phase domain spectra, which shows  $-10^\circ$  phase delay at 1758  $\text{cm}^{-1}$  (Figure 1b), indicating AA is formed after flowing ethanol. At the same time, the columnar O-H stretching at 3572  $\text{cm}^{-1}$  from HAP is being consumed, which can also be observed at

1630  $\text{cm}^{-1}$  (O-H bending) in phase and time domain spectra, suggesting that the columnar hydroxyl group could act as basic site to abstract hydrogen from ethanol. Butanal and CA appear only in trace amounts in the mass spectra (Figures 1c and 1d), in accordance with a previous report claiming that soon after it is formed, CA rapidly undergoes hydrogenation to COH. Overall, we can now monitor AA formation and columnar hydroxyl group consumption in MES-DRIFTS-MS simultaneously.

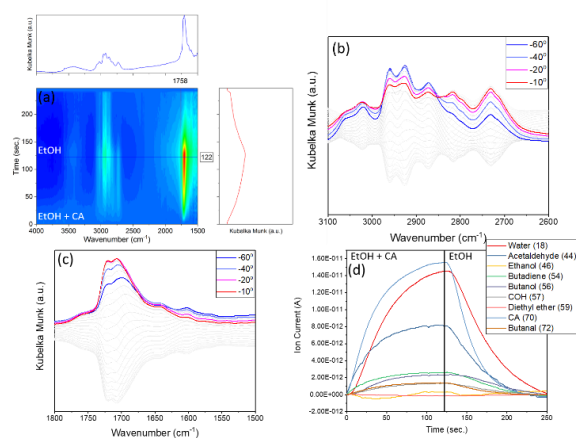
When we co-fed AA with ethanol and carrier gas in the first half period and flowed only ethanol with carrier gas in



**Figure 2.** Modulation experiment between EtOH/AA(3:1) and EtOH flow over hydroxyapatite at 330°C. a) Time-domain, b,c) Phase-domain DRIFTS spectra, d) Recorded MS spectra.

aromatic coke which appears at 1602 and 1576  $\text{cm}^{-1}$  with a greater phase delay and time delay (Figure 2a).

In order to understand hydrogen transfer from ethanol to CA, which has been proposed previously in the literature, we co-fed CA with ethanol in the first half period and flowed only ethanol with carrier gas in the second half period. The



**Figure 3.** Modulation experiment between EtOH/CA(3:1) and EtOH flow over hydroxyapatite at 330°C. a) Time-domain, b,c) Phase-domain DRIFTS spectra, d) Recorded MS spectra.

transfer from ethanol to CA. Furthermore, the C=C stretching of COH which is hydrogenated from CA can also be seen at 1650  $\text{cm}^{-1}$ , showing  $-40^\circ$  delay. In conclusion, we can use DRIFTS and MS as complimentary techniques to investigate the reaction simultaneously, leading to more complete insights for surface catalyzed reactions.

This grant was used to support one graduate student who constructed the setup and performed the MES FT-IR experiments for ethanol coupling reactions, including aldol condensation on surface catalyzed reactions. The work, ethanol coupling to *n*-butanol by hydroxyapatite, by using MES-DRIFTS-MS is now in preparation for submission.