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14. ABSTRACT
Getting molecular-level insights into processes at solid interfaces is a highly challenging task. In this work, we use Modulation Excitation Spectroscopy in combination with Infrared Spectroscopy to gain such insights on solid-liquid and solid-gas interfaces. We studied the cyclization of citronellal and the coupling of ethanol forming butadiene as case studies of reactions of contemporary interest to further develop the technique, the setups and test its applicability. We obtained intriguing results that helped us propose molecular-level reaction mechanisms that rationalize literature data. This work has lead to two publications in peer reviewed journals and allowed us to

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## Report Title

Final Report: Insights in catalytic transformations at the solid-liquid interface using MES-ATR-IR Spectroscopy

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Getting molecular-level insights into processes at solid interfaces is a highly challenging task. In this work, we use Modulation Excitation Spectroscopy in combination with Infrared Spectroscopy to gain such insights on solid-liquid and solid-gas interfaces. We studied the cyclization of citronellal and the coupling of ethanol forming butadiene as case studies of reactions of contemporary interest to further develop the technique, the setups and test its applicability. We obtained intriguing results that helped us propose molecular-level reaction mechanisms that rationalize literature data. This work has lead to two publications in peer-reviewed journals and allowed us to further advance the technique.

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| 08/12/2016 | 3.00 | . Understanding Heterogeneous Lewis Acid Catalysis using ATR-IR Modulation Excitation Spectroscopy, Catalysis Club of Chicago Spring Symposium. 17-MAY-16, Naperville, IL. : , |
| 08/12/2016 | 4.00 | . Understanding Heterogeneous Lewis Acid Catalysis using ATR-IR Modulation Excitation Spectroscopy, 252nd American Chemical Society National Meeting & Exposition. 23-AUG-16, Philadelphia, PA. : , |
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| Philipp Müller | 1.00 | |
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| **Total Number:** | **1** | |

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## Inventions (DD882)

## Scientific Progress

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## Technology Transfer

# Final progress report: Insights in catalytic transformations at the solid-liquid interface using Modulation Excitation Attenuated Total Reflection IR Spectroscopy

*Philipp Müller, Prof. Ive Hermans, University of Wisconsin – Madison, Department of Chemistry, Department of Chemical and Biological Engineering*

*08/10/2016*

This document gives an overview over the progress made in the project titled "Insights in the catalytic transformations at the solid-liquid interface using Modulation Excitation Attenuated Total Reflection IR Spectroscopy" that is supported by the US Army Research Office under grant W911NF-15-1-0134.

In our initial proposal, as also mentioned in the title, we suggested the use of Attenuated-Total-Reflection-Infrared-Spectroscopy (ATR-IR) in combination with Modulation Excitation Spectroscopy (MES) to investigate solid-liquid reactions. As a case study, we chose the cyclization of citronellal to isopulegol catalyzed by different stannosilicates, to illustrate the potential of this technique on a system of contemporary interest. However, as the Army Research Office had a bigger interest in interactions at the gas-solid interface, we then changed the focus of the project to investigate the coupling of ethanol to form butadiene. By the time the project started, we had already obtained good data on the liquid-phase reaction. The progress in the liquid-phase helped tremendously in developing the gas-phase setup, which is why these results will briefly be discussed in the first paragraph.

*Insights into the Complexity of Heterogeneous Liquid-phase Catalysis: Cyclization of Citronellal*

We investigated the cyclization of citronellal by a combination of reactivity measurements in a batch reactor and ATR-IR-MES experiments. We found vast differences in activity and selectivity between the microporous Sn-Beta and the mesoporous Sn-SBA-15 catalysts in toluene and acetonitrile as solvents. Hence, we decided to study these two materials spectroscopically. In Figure 1 a), the time-domain spectra, i.e. the spectra that are actually measured during a modulated adsorption of citronellal in toluene on SBA-15 are shown. In Figure 1 c), the phase-domain spectra, i.e. the spectra after mathematical treatment and transformation to the phase-domain are shown. It can be seen, that the noise level is very low in these spectra. Furthermore, the assignment of phase-delays to the spectra allows for an easier (semi)-quantitative analysis of consecutive reaction steps. For example in Figure 1 d), at a phase-delay of 30° Citronellal (green) appears in the liquid-phase. Then at a delay of 50° Citronellal adsorbs on the Sn site and finally at 70° the product isopulegol can be observed. Furthermore, the differences in surface coverage between the microporous Sn-Beta (Figure 1f) and the mesoporous Sn-SBA-15 (Figure 1d) is one reason for the differences in activity. Further experiments, that are not shown here, allowed us to get conclusions about several effects that influence the activity of these materials, as summarized in Figure 2.

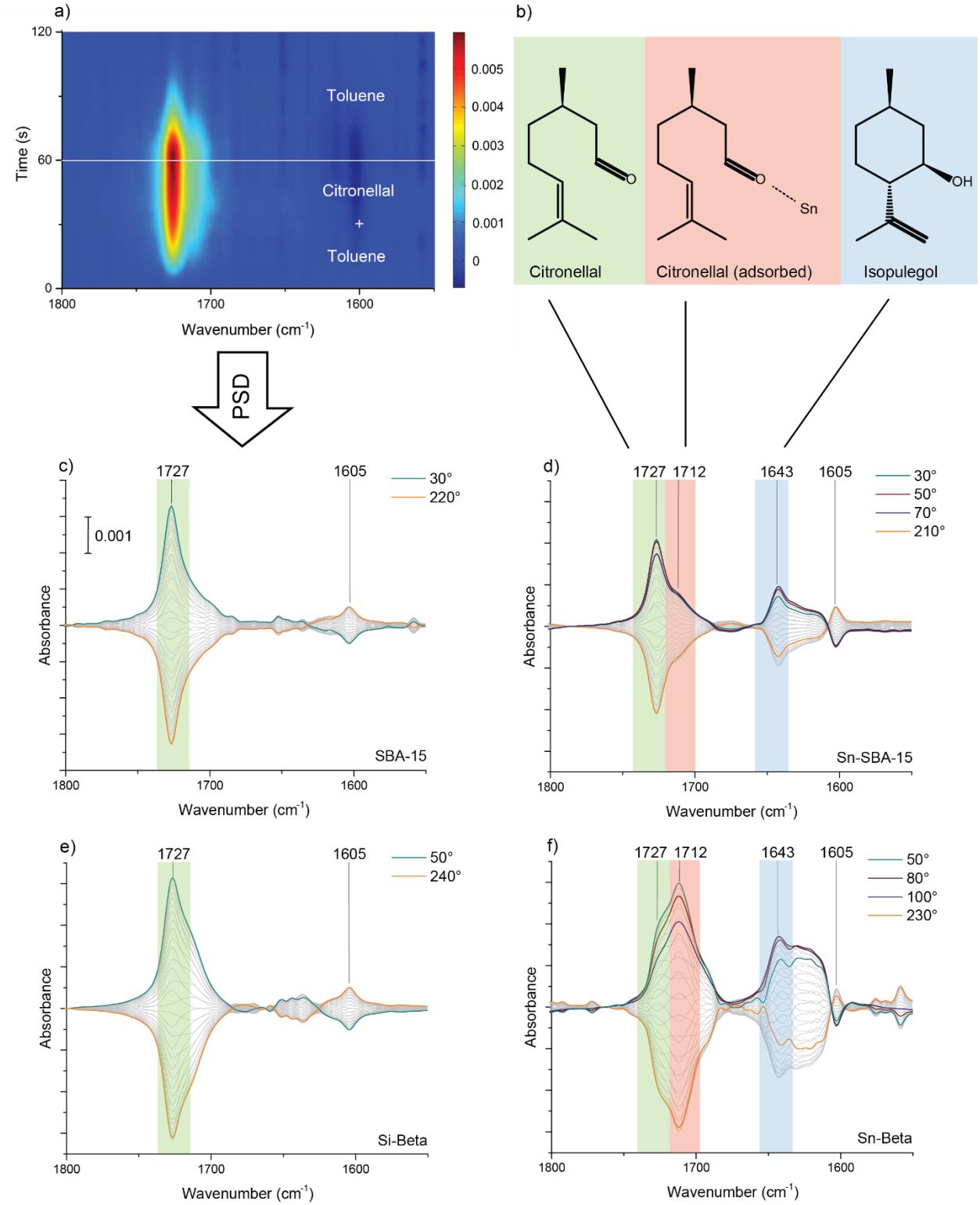


**Figure 1**. a) Time-domain spectra for the modulation of 20 mM citronellal in toluene at 333 K for SBA-15, b) Schematic representation of the most important molecular structures and their assignment, Phase-domain transformed spectra for c) SBA-15, d) Sn-SBA-15,e) Si-Beta and f) Sn-Beta.

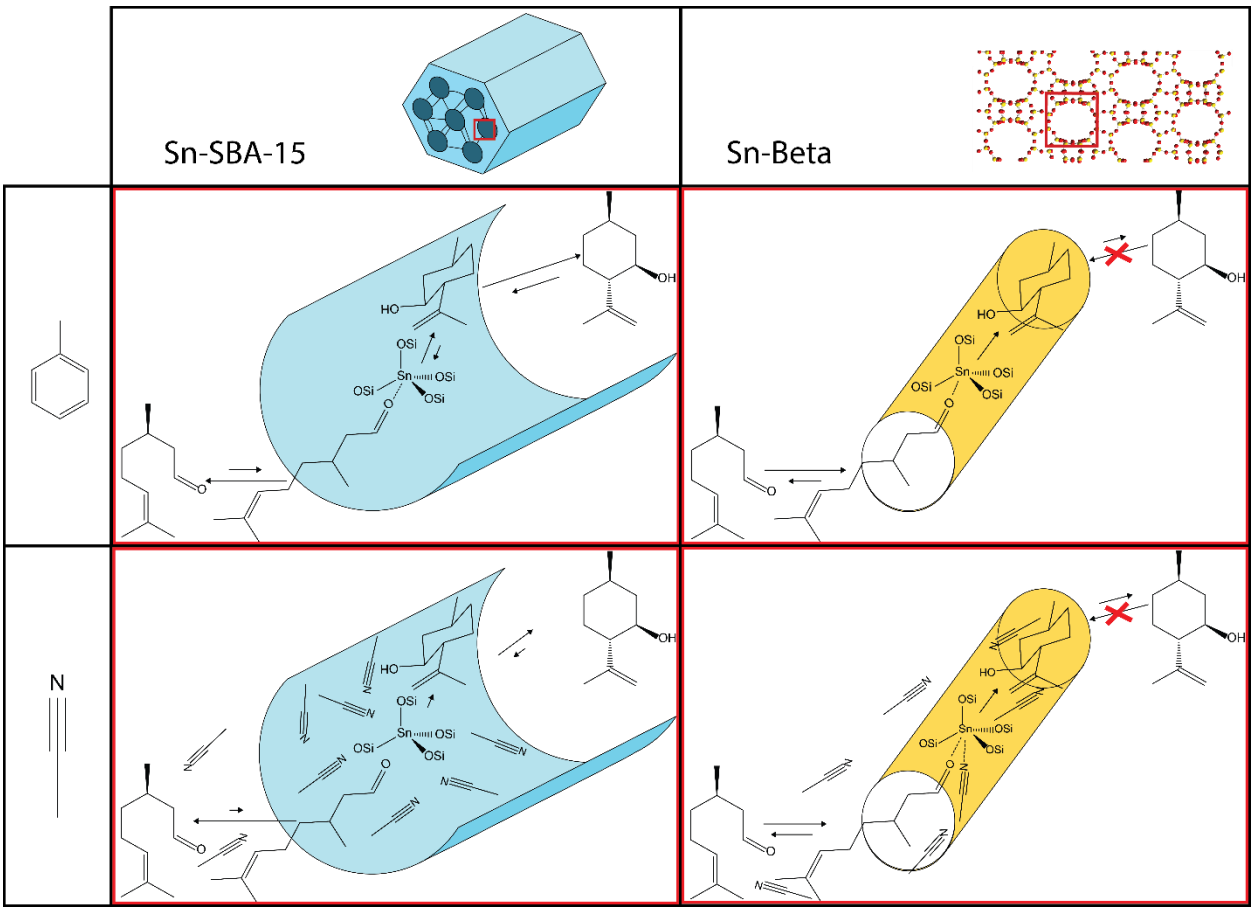


**Figure 2** Representation of effects occurring during the cyclization of citronellal over Sn-SBA-15 and Sn-Beta in the presence of acetonitrile and toluene.

The results of this study have been published in ACS Catalysis.[1]

*Insights into the Complexity of Heterogeneous gas-phase Catalysis: Ethanol Coupling to Butadiene*

With the knowledge obtained from setting up the liquid-phase experiments, we developed the setup depicted in Figure 3 for our gas-phase applications. It consists of two independent mass flow controllers (MFC) that are connected to an inert gas (He). The gas is then directed into a T-piece that is connected to a syringe pump and allows for the evaporation of liquid substrates. Consequently the gases flow through a newly purchased four-ports-two-way valve (VICI Inc.) that can be controlled manually or electronically. One of the gas-flows is passing through the Diffuse Reflectance Infrared Spectroscopy (DRIFTS, Pike Technologies Inc.) accessory, while the other one goes to the vent. At the outlet of the DRIFTS accessory, a mass spectrometer (MS) is connected and simultaneously records specific masses.

One of the most difficult parts of the setup was the evaporation of the liquid substrates. So far, the state-of-the-art technique to do this was a simple bubbler that would saturate the gas-stream.[2] However, as there is only little control over the actual gas-phase concentration, we decided to use a syringe pump with an evaporation system instead. To achieve this, we built a custom-made connection between the needle of a 5 mL syringe and a 1/8” Swagelok T-piece. Also the chosen gas and liquid flow rates are crucial for a

successful experiment. When the gas flow is too high, the contact time with the catalyst is low and so is the conversion, but when it is too low the evaporation process is not complete. The appropriate ratio was finally found empirically.

One prerequisite of a successful MES experiment is having a low dead volume. We achieved this by keeping the stainless steel tubing as short as possible. Furthermore, the tubing has to be heated and insulated very well in order to keep all of the compounds in the gas-phase. It was a challenge to achieve this, as the tubes get contaminated with condensation products if the heat insulation is not good enough, which leads to unpredictable IR and MS signals.

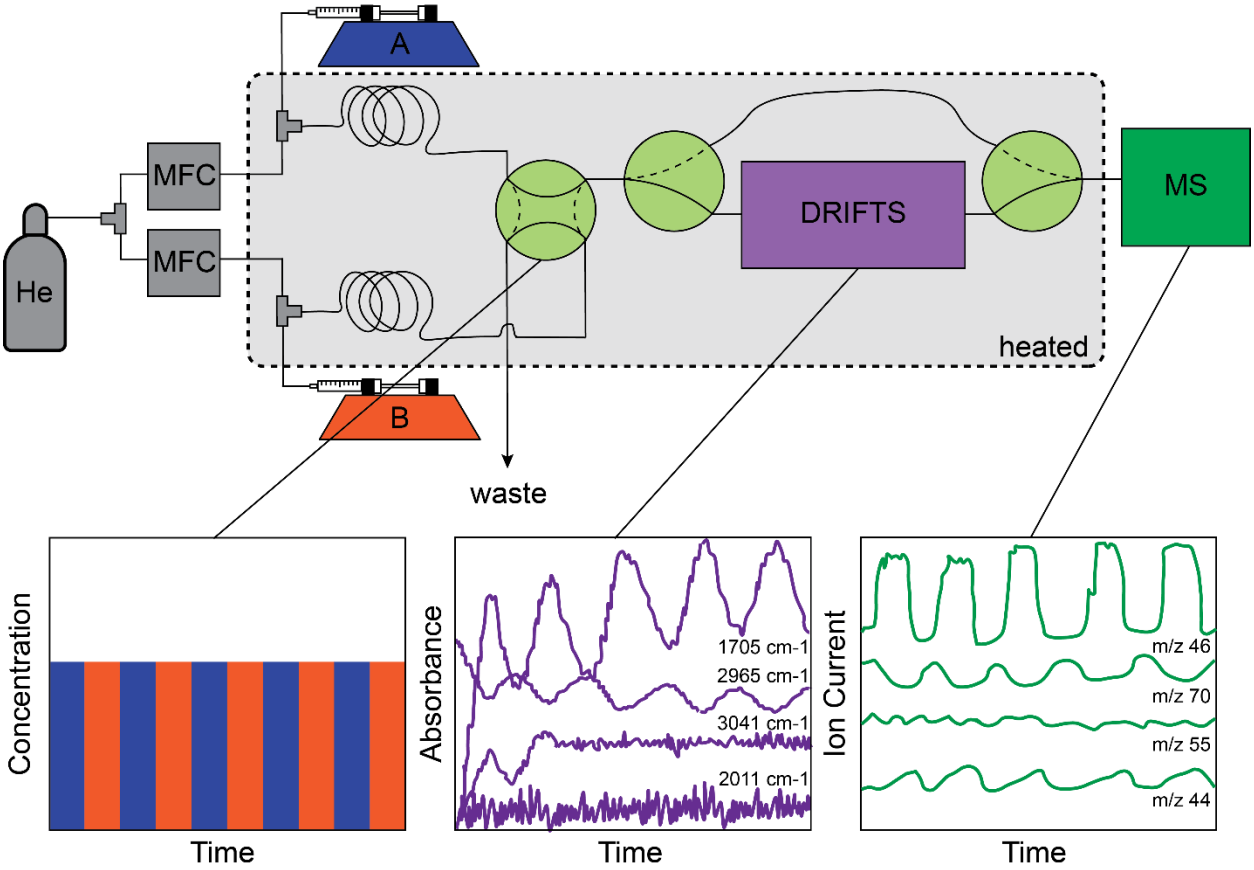


**Figure 3.** Schematic overview of the DRIFTS-MS setup. By using two syringe pumps and heated coils that enter a two-position-four-way valve, the gas-phase composition can be modulated between substrates A and B. Depending on the chosen position, either flow A or B flows through the DRIFTS accessory followed by the online mass spectrometer. In addition, two three-way-valves allow the substrates to bypass the DRIFTS accessory to ensure steady gas-phase concentrations prior to measurements.

Once the setup was optimized, and reproducible spectra were obtained, we started investigating the reaction we had proposed, namely the ethanol coupling to butadiene (BD) over Ta-containing catalysts. During the development of the setup, a manuscript was published by Kyriienko et al.[3] that used Ta-BEA zeolites that were more active and selective toward BD than the state-of-the-art Ta/$SiO_2$. Hence, we decided to synthesize and characterize this material and use it for our study.

We performed several experiments to understand the generally proposed and complex reaction pathway depicted in Figure 4, and to figure out the origin of the different intermediate species.

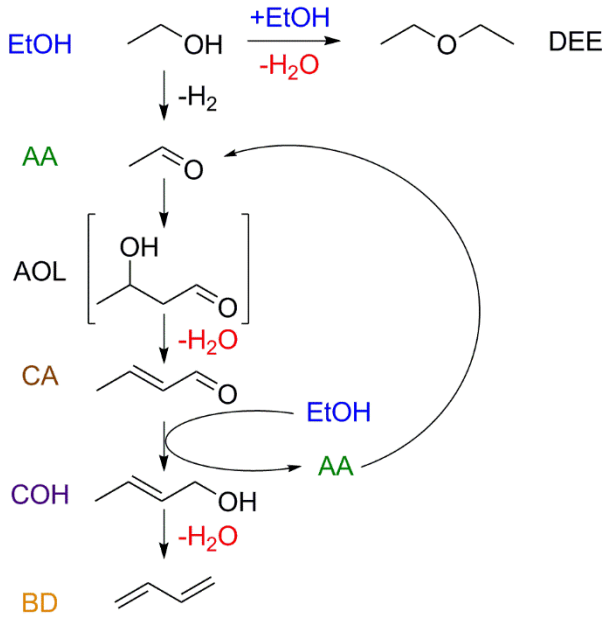


**Figure 4** Reaction pathway for the coupling of ethanol to 1,3-butadiene. Ethanol (EtOH) is dehydrogenated to acetaldehyde (AA), which undergoes self-condensation to form the unstable intermediate acetaldol (AOL). Dehydration of AOL leads to the formation of crotonaldehyde (CA) that undergoes a Meerwein-Ponndorf-Verley (MPV) reduction with ethanol as hydrogen donor producing crotyl alcohol (COH). Crotyl alcohol can then be dehydrated to yield the desired product 1,3-butadiene (BD). Alternatively, an initial dehydration reaction between two molecules of EtOH leads to the by-product diethyl ether (DEE).

As an example of some experiments, we show the modulation between a mixture of EtOH and acetaldehyde (AA) and EtOH in Figure 5. In a) the mass spectrometry signals are shown and in b) the corresponding IR spectra. It can clearly be seen that the presence of AA is required to form BD. Furthermore, we found an intermediate with a specific IR band at 1690 $cm^{-1}$. We attribute this band to a "crotoxy" intermediate, i.e. an adsorbed crotonaldehyde intermediate that forms in the presence of EtOH and crotonaldehyde (vide infra). This surface intermediate seems to be crucial for forming BD and has never been observed before. When performing the reverse experiment, i.e. first saturating the surface with a mixture of EtOH and AA and then switching to pure AA, the MS signals look quite different. The switch to pure AA immediately triggers higher CA concentration, due to fast AA coupling. As the surface is still saturated with ethoxy species from the half-period before, the formed CA can readily be transformed to Crotyl alcohol and then dehydrated to BD. Also in this case, the surface intermediate at 1690 $cm^{-1}$ was present.

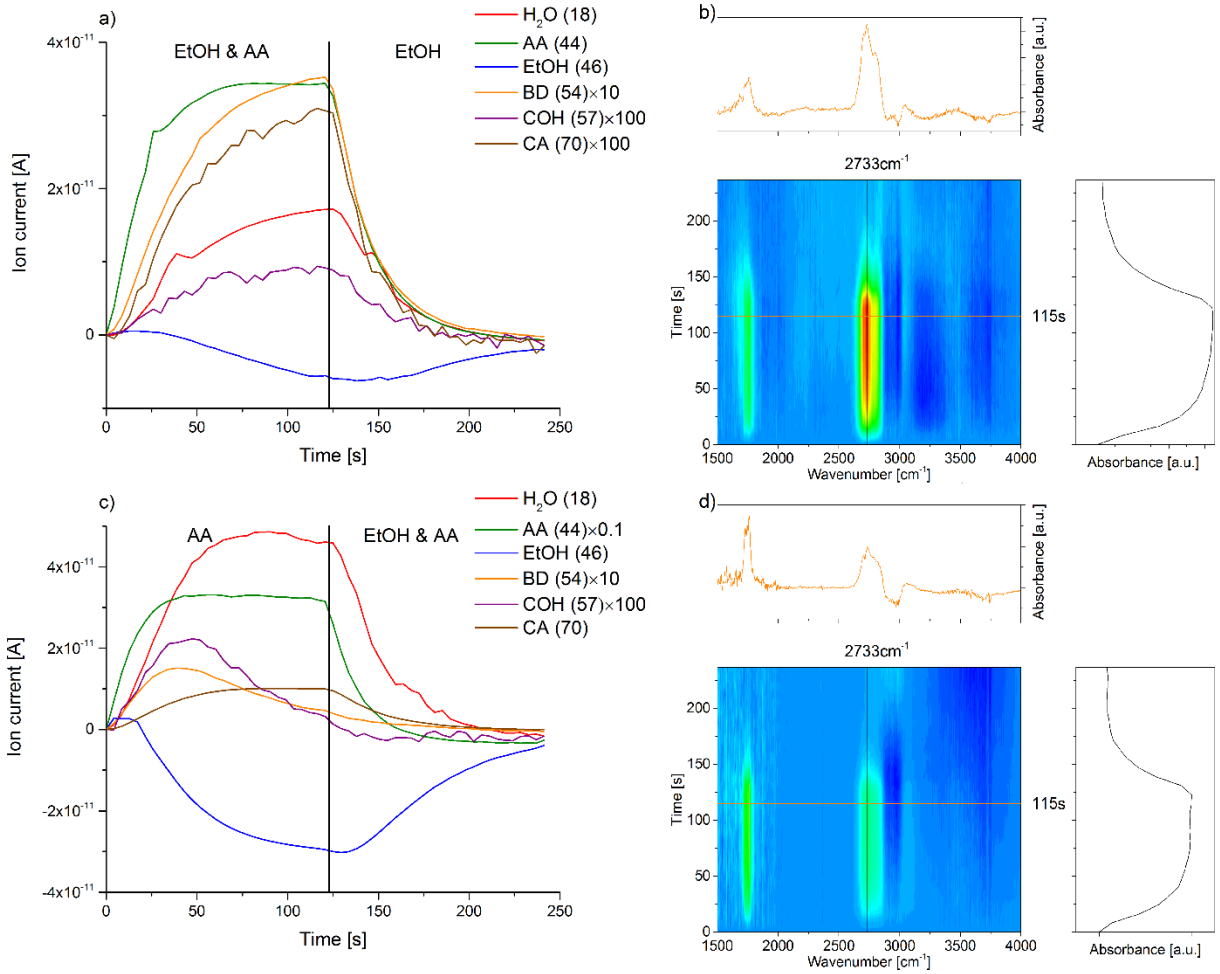


**Figure 5.** Modulation experiments between pure EtOH in He and a 3:1 mixture of EtOH/AA over Ta-BEA at 300°C. a) shows the recorded MS signals of a modulation experiment, where the surface was first saturated with EtOH followed by periodically switching to EtOH/AA. b) shows the corresponding infrared spectra. In c) the surface was first saturated with the reaction mixture EtOH/AA followed by pure AA flow, and d) shows the corresponding infrared spectra. The switch from one flow to another was done after 120 seconds as indicated by the black line. Three periods were averaged when quasi steady-state was reached.

Further experiments with the intermediate CA, methanol instead of EtOH and also isotopically labeled EtOH helped us propose the reaction mechanisms given in Figure 6.

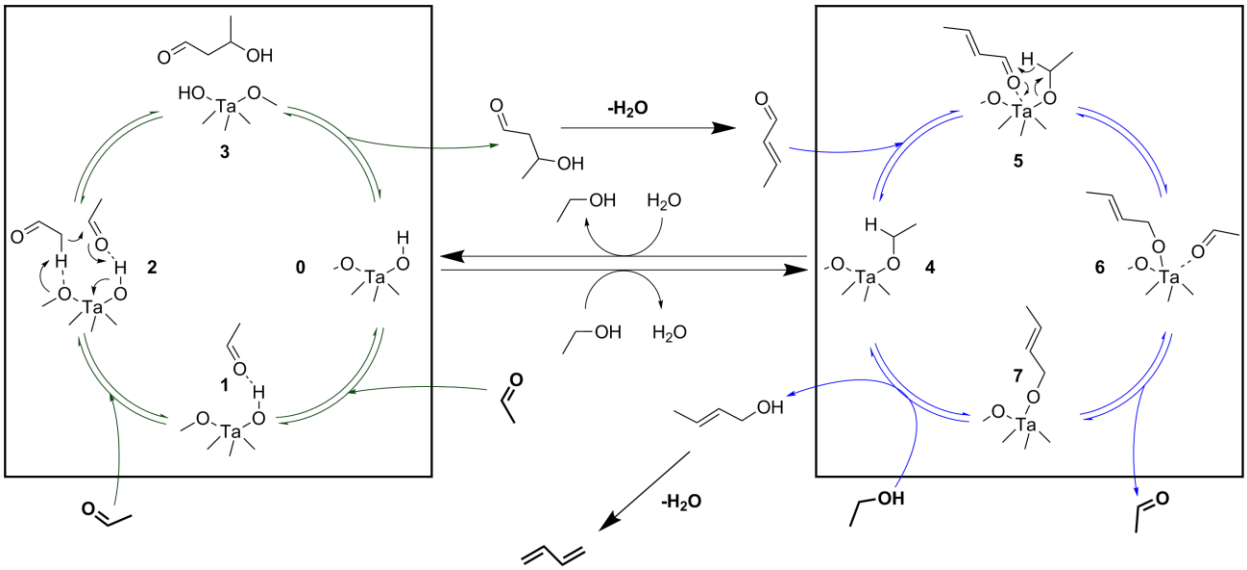


**Figure 6.** Tentative mechanism of the coupling of acetaldehyde over Ta-BEA on the left, followed by the MPV reaction between EtOH and CA on the right. The molecules represented in bold show the overall stoichiometry of the reaction: 2 AA + EtOH → BD + AA + 2 $H_2O$

First, two AA molecules coordinate to the Ta site (**0**→**1**, **1**→**2**) through hydrogen bonding. Then, the proposed mechanism goes through an eight-membered ring transition state (**2**→**3**) and forms the unstable intermediate AOL that is quickly dehydrated to CA.

The second step, *i.e.* the MPV reaction between EtOH and CA, is thought to be catalyzed by tantalum.[4] It is well known that ethoxy species can be formed on silica.[5] As we saw with our isotopic labelling experiments, such species also form on Ta-BEA and are involved in the formation of COH. Since Ta-OH sites are also more acidic than silanols,[6] the first step in our proposed MPV reaction mechanism is therefore the formation of an ethoxy species on a Ta site (**4**).

Upon the adsorption of EtOH two negative IR signals at 3740 and 3745 $cm^{-1}$ appeared that could be attributed to Si-OH and Ta-OH and are indicative of their consumption. Furthermore, we observe the formation of water in the MS corroborating the formation of structure (**4**). In a second step, CA coordinates to the Ta site leading to intermediate (**5**). The reaction would then go through a six-membered ring transition state, where hydrogen transfer leads to an adsorbed AA (**6**). AA can then desorb from the site, as observed in the MS, and potentially undergo coupling with another AA molecule itself. An incoming EtOH molecule displaces COH from the active site closing the catalytic cycle (**7**→**4**).

Based on our data and interpretation, it appears that it is highly important to have precise control over the ratio of different adsorbed species in order to maximize the production of BD. A high AA concentration will lead to large amounts of CA, which will not react further. The additional water that is formed in the dehydration of AOL to CA shifts the equilibrium away from the reactive ethoxy species reducing the contribution of the right catalytic cycle that forms BD. When, on the other hand, the EtOH concentration is too high, not enough CA will be produced as the Ta sites will be covered with EtOH such that AA cannot

react efficiently anymore. Hence, these findings explain why the BD productivity is so sensitive towards changes in the feed composition.[3,4,7,8]

More detailed results of this work were submitted to ACS Catalysis.[9] The manuscript is attached.

*Conclusions & Future Work*

With these two case studies in the liquid- and the gas-phase, we were able to show how useful modulation excitation spectroscopy can be when trying to understand processes at solid interfaces on a molecular level.

In the liquid-phase study, we gained insights into solvent and confinement effects occurring at the solid-liquid interface for different micro- and mesoporous materials. We were able to follow the reaction as it was happening, i.e. diffusion of the substrate to the active site, adsorption to the active site, reaction, desorption and diffusion out of the pores. Furthermore, we found that it is important to study these systems under true reaction conditions. Other commonly used characterization techniques use gaseous probe molecules that adsorb to the active site.[10] Our data suggests that these studies are not sufficient to capture the complexity of heterogeneously catalyzed liquid-phase reactions. The use of MES-ATR-IR proves to be a unique tool to probe dynamics at the solid-liquid interface with high sensitivity to get molecular-level insights under reaction conditions.

In the gas-phase study, we gained insights into interactions of ethanol, acetaldehyde and intermediate coupling products in the production of butadiene with the heterogeneous catalyst under reaction conditions. To the best of our knowledge, this is the first dynamic operando spectroscopic study of this reemerging reaction. Distinguishing between the various possible pathways in this reaction is a demanding task. The simultaneous measurement of gas-phase and adsorbed species using our specifically developed setup provided valuable information in that regard. The interpretation of this data helped us proposing a reaction mechanism that rationalizes the different pathways that occur simultaneously and explains some observations found in literature.

Due to the high complexity of this reaction and the unusual non-square-wave shape of some of the MS and IR signals, we were unfortunately unable to perform the microkinetic analysis we intended to do. We believe that choosing a simpler reaction such as CO oxidation on metal surfaces would make the microkinetic analysis easier and could tell us, if the setup is robust enough to give reproducible results that are comparable to literature values. Furthermore, the heating element of the DRIFTS accessory would need to be optimized as there likely are some temperature gradients and fluctuations within the sample.

Nevertheless, the developed setup already gave exciting results and we are going to develop it further and apply it to other systems of interest. We would like to express our sincere gratitude for supporting this research.

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