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## Research Area

Catalysis is the process of accelerating a chemical reaction by using a catalyst, a substance that does not undergo a permanent chemical change as it is not consumed during the mechanism. In this study, we focus on heterogeneous catalysis, where the catalyst and the reactants are not present in the same phase. These reactions can include, but are not limited to, gases, liquids, or both at the catalytic surface. Doing so allows the reactants to be adsorbed onto the surface to interact with the catalyst, improving the overall reactivity. This field is committed toward enhancing chemical processes by lowering the activation energy barrier, resulting in reaction rate acceleration, milder operating conditions, and increased selectivity. At UTSA, the heterogeneous catalysis group applies these concepts to energy and fuel related reactions.

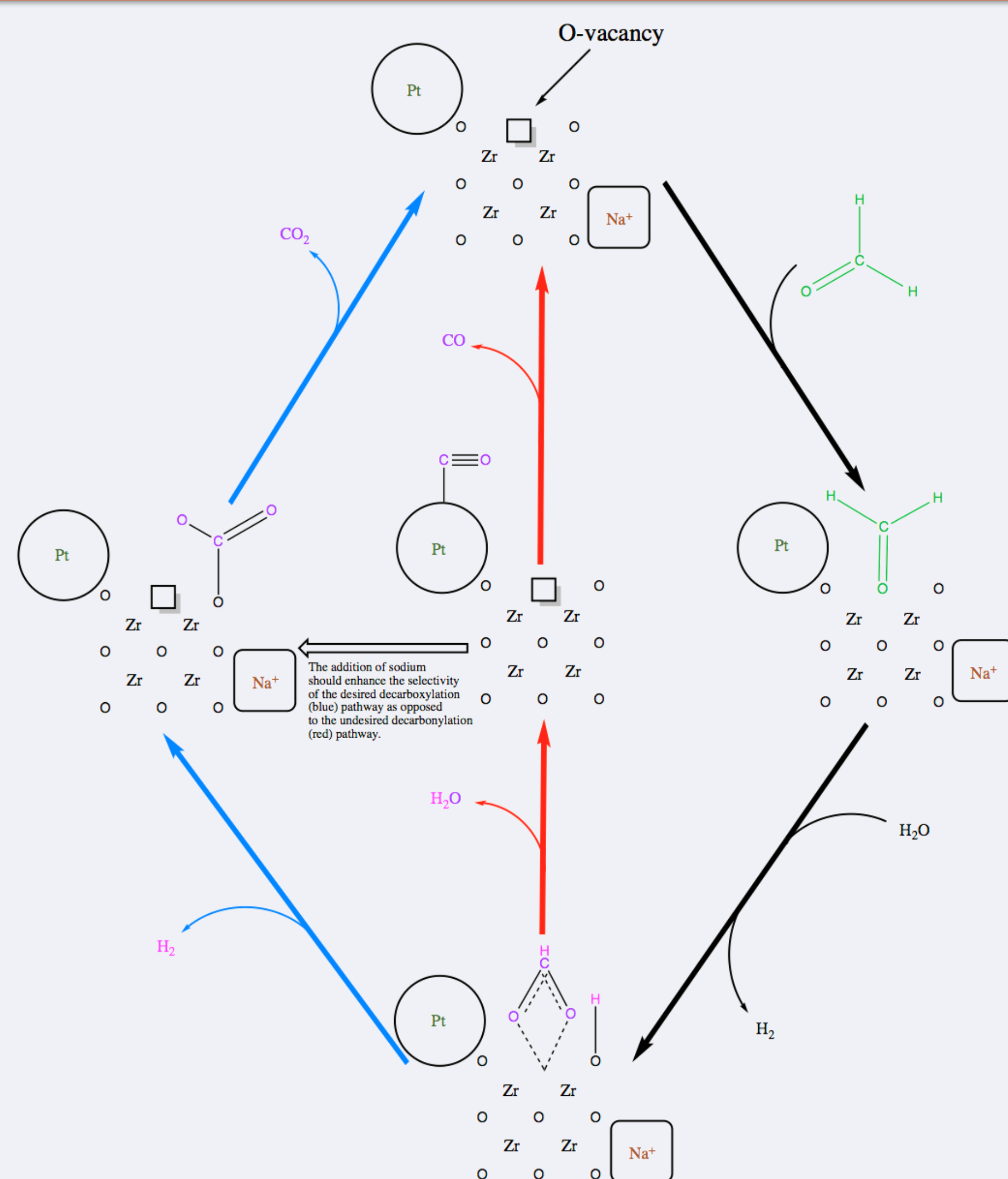
## Background

Steam reforming may be characterized as a process in which hydrocarbons (e.g., derived from natural gas) are heated with steam, generally in the presence of a catalyst to improve the rate of reaction and the selectivity to H<sub>2</sub>. Steam reforming is used extensively for hydrogen generation, not only to produce H<sub>2</sub> from nonrenewable resources, but also from renewable feedstocks such as bioethanol. Moreover, liquid chemical carriers such as formaldehyde and methanol can be synthesized from synthesis gas (CO and H<sub>2</sub>) produced from steam reforming and partial oxidation of methane or bioethanol, or from the gasification of coal or biomass. The transition from nonrenewable resources to more environmentally friendly alternatives is vital moving forward as fossil resources are continuously depleting. Although hydrogen has a high energy density per mass, hydrogen storage is an issue, due to its low energy per unit volume in the vapor phase. This has led to researching liquid chemical carriers of hydrogen, molecules that can readily generate hydrogen through reaction with steam. In methanol and ethanol steam reforming (MSR and ESR), an observation was made that alkali promoters promote forward decomposition of the formate (MSR) or acetate (ESR) intermediate to CO<sub>2</sub>, which improves H<sub>2</sub> selectivity. However, with the absence of alkali, significant reverse decomposition of formate/acetate occurs, leading to CO formation and lower H<sub>2</sub> selectivity. Formaldehyde can be used as a H<sub>2</sub> carrier; moreover, it is a likely intermediate in the steam reforming of methanol. Therefore, it is important to improve the H<sub>2</sub> selectivity of formaldehyde steam reforming.

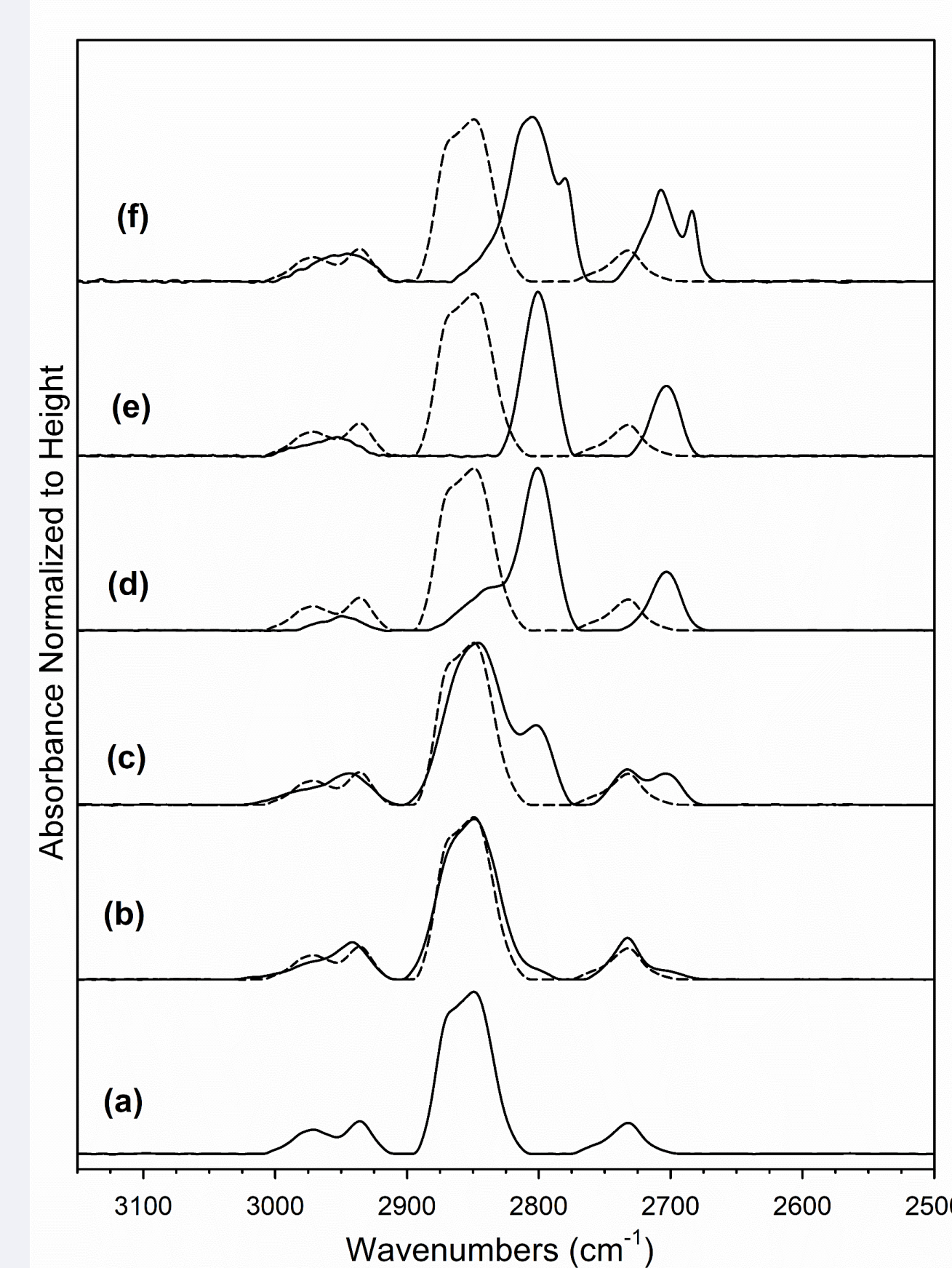
## Objectives

- Examine promoting effects of sodium (Na) for formaldehyde steam reforming
- Determine the optimal loading of sodium for FSR
- Investigate the decomposition selectivity of a potential liquid chemical carrier of H<sub>2</sub> (formaldehyde) for portable power and medical applications
- Discover the impact of sodium loading on Pt nanoparticles on the catalytic surface
- Investigate the electronic effect of sodium, which influences the structure, reactivity, or properties of a molecule, on the intermediate formate C-H bond.

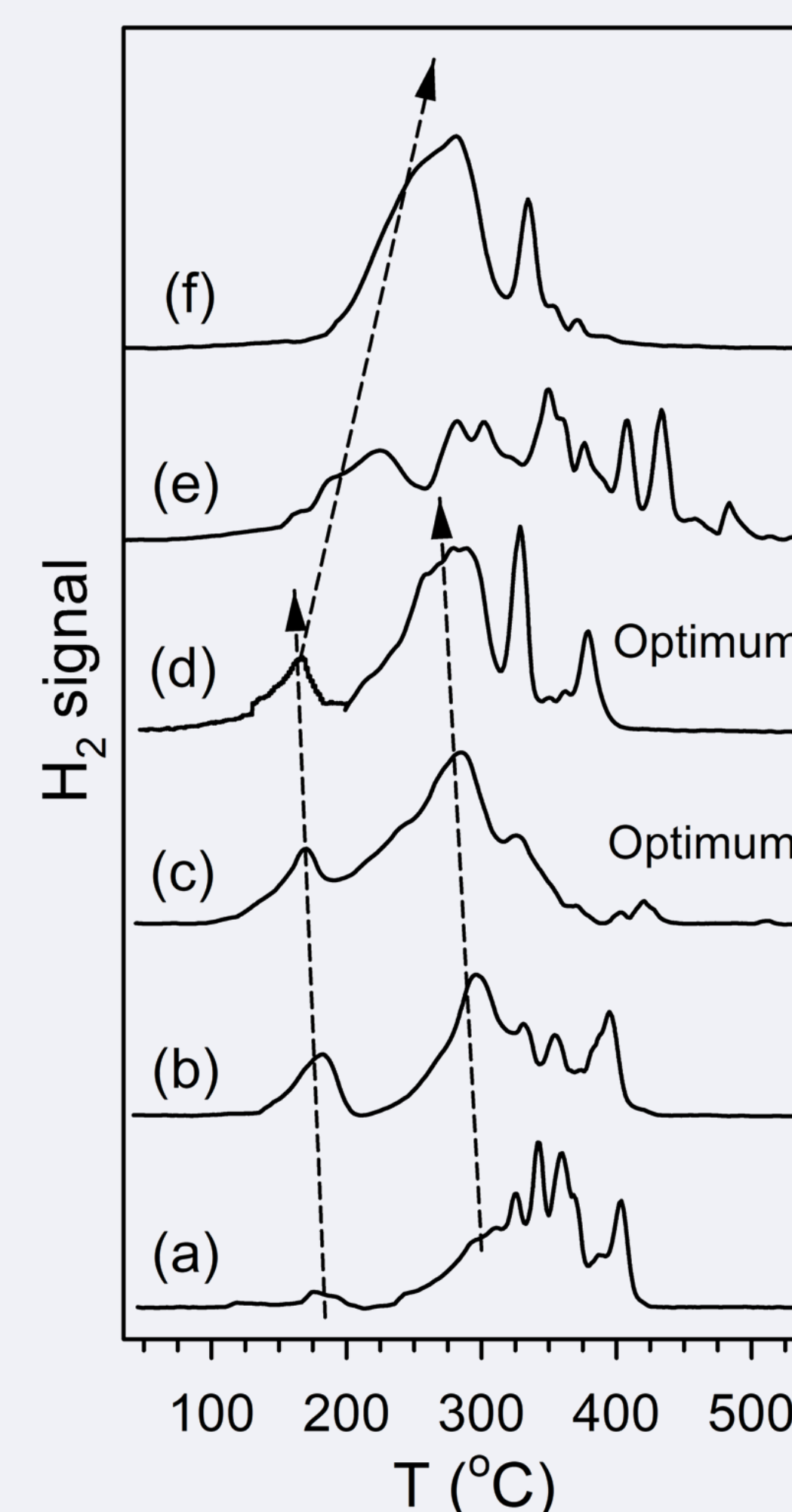
## Results



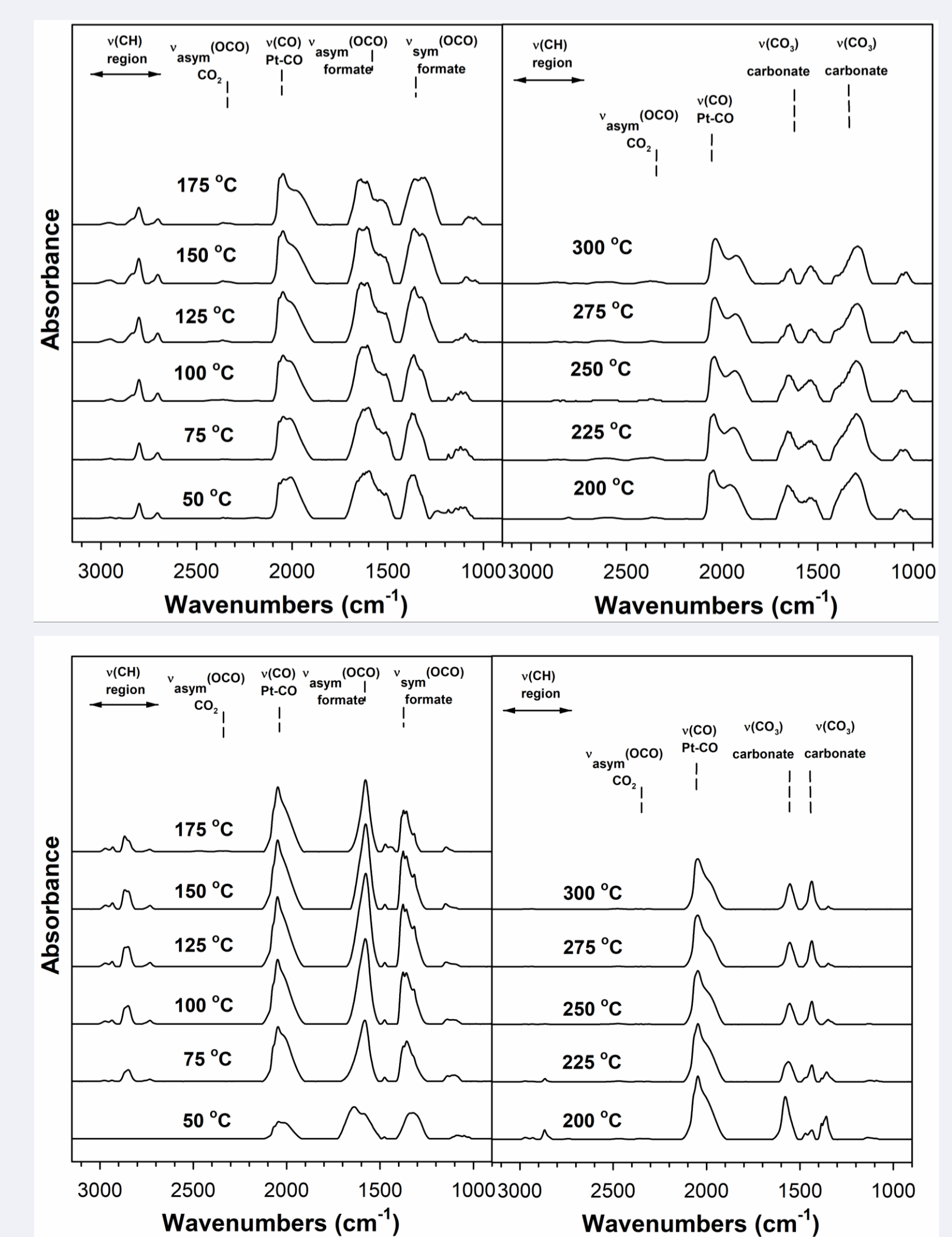
**Figure 1:** Simplified formaldehyde steam reforming mechanism using an activated Pt/ZrO<sub>2</sub> catalytic surface.



**Figure 2:** Absorbance of the formate  $\nu(\text{CH})$  band region normalized to height of band on 2%Pt/ZrO<sub>2</sub>, including: (a) 2%Pt/ZrO<sub>2</sub>, (b) 0.5%Na-2%Pt/ZrO<sub>2</sub>, (c) 1.0%Na-2%Pt/ZrO<sub>2</sub>, (d) 1.8%Na-2%Pt/ZrO<sub>2</sub>, (e) 2.5%Na-2%Pt/ZrO<sub>2</sub>, and (f) 5.0%Na-2%Pt/ZrO<sub>2</sub>. (Dashed lines) 2%Pt/ZrO<sub>2</sub>, reference.



**Figure 3:** TPD-MS summary showing the temperature at which H<sub>2</sub> is coming off over time (bottom step of the mechanism to the proceeding step). See Figure 2 for the legend.



**Figure 4:** Comparison of the DRIFTS analysis of the optimal loading at 1.8 wt.% Na from 50-300°C (top) and that of unpromoted 2%Pt/ZrO<sub>2</sub> (bottom).

- Figure 1** outlines the simplified formaldehyde steam reforming mechanism using an activated Pt/ZrO<sub>2</sub> catalytic surface. One step of the mechanism is the breaking of the formate C-H bond. Addition of sodium assists in weakening this bond, which is supported by the redshift of the  $\nu(\text{CH})$  band in Figure 2. As such, H<sub>2</sub> formation and decarboxylation of formate is favored (blue pathway) instead of decarbonylation and H<sub>2</sub>O formation (red pathway), thereby improving the selectivity.
- Figure 2** summarizes the absorbance of the formate  $\nu(\text{CH})$  band at different loading quantities with respect to the reference. We observe that the formate band shifts to lower wavenumbers at higher loadings, indicating that the bond is weakening.
- Figure 3** depicts the TPD-MS data retrieved at various loadings, highlighting the temperatures at which H<sub>2</sub> is being released. For catalysts that facilitate formate decomposition, H<sub>2</sub> peaks appear at lower temperatures, providing an optimal loading around 1 - 1.8 wt.% Na. Sodium begins to cover the catalytic surface, especially Pt, at loadings higher than the optimal, resulting in a decreased rate of formate decomposition.
- Figure 4** visually describes how at the optimal loading of alkali, there exists enough alkali to weaken the formate C-H bond, which can be observed through the band shift and the enhanced decomposition rate. Additionally, there is not excessive alkali to cover the Pt nanoparticles since the Pt-CO bands are still present, in contrast to the case of higher loadings where the band is virtually nonexistent.

## Future Plans

Liquid chemical carriers of hydrogen may become of great importance to this field. This catalyst could potentially enhance H<sub>2</sub> selectivity from formaldehyde, as one such H<sub>2</sub> chemical carrier. Methanol is a product of syngas conversion (CO + H<sub>2</sub>) and syngas can be derived from natural gas, coal, and biomass through partial oxidation, gasification, and steam reforming reactions. Because formaldehyde is a likely intermediate in methanol steam reforming, the results of this investigation are also important from that standpoint. We plan to continue to investigate ways to enhance H<sub>2</sub> selectivity from FSR as a liquid chemical carrier of H<sub>2</sub>, and as it may apply to methanol steam reforming. One avenue of research is optimizing the type and loading of alkali dopants.

## Skills and Experience

- Diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS)
- Temperature-programmed desorption mass spectrometry (TPD-MS)
- Data processing and analysis through Microsoft Excel and OMNIC FTIR software

## What I learned

After analyzing the DRIFTS and TPD-MS data, I concluded that the optimal sodium loading was likely ~1.8 wt.% for the tested catalysts. Additionally, I learned that electronic weakening of the formate C-H bond will likely lead to a higher selectivity of H<sub>2</sub> during FSR as revealed by infrared spectroscopy and TPD-MS results. Furthermore, I learned different reactions involved in the production of hydrogen, including steam reforming of hydrocarbons and oxygenates, as well as the water-gas shift reaction.

## Acknowledgements

I would personally like to recognize and thank Dr. Gary Jacobs for including me in the heterogeneous catalysis research group and presenting me with the opportunity to further assist in advancing his primary research of interest. I would also like to thank my co-authors for their helpful insights.

## References

Martinelli, M.; Jacobs, G.; Graham, U.M.; Davis, B.H., "Methanol steam reforming: Na doping of Pt/YSZ provides fine tuning of selectivity," Catalysts 7 (2017) 148 (14 pages), MDPI publishing, Special Issue in honor of Calvin H. Bartholomew.