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Research Area

Heterogeneous Catalysis for Energy Applications

Background

The Ethanol Steam Reforming (ESR) reaction ($C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$) is a significant industrial process to generate a pure hydrogen for use in various applications that require hydrogen, especially PEM fuel cell applications. In fact, hydrogen nowadays is considered to be the energy carrier of the future because of its carbon-free energy, which is important for lowering line sources of emissions, including harmful byproducts of internal combustion engines used in transportation and portable power applications. In this project, the noble metal platinum (Pt) was impregnated into the zirconia (ZrO₂) support because, despite being costly, Pt enhances activity, stability, and coke resistance of the catalyst. This Pt/ZrO₂ system, when promoted with the alkali metal potassium (K), causes ESR to selectively proceed in the forward (desired) direction, increasing hydrogen production. In previous studies, our group showed that changing the loading of sodium in this catalyst system affected the rate and selectivity of hydrogen production. To further this work, I investigated several loadings of potassium to find the “sweet-spot” for hydrogen selectivity and production rate during ESR for Pt/ZrO₂.

Objectives

1. Last semester, we found that at optimum loading, potassium (K) resulted in an electronic weakening of the formate C-H bond in low temperature water-gas shift (LTS), while keeping platinum (Pt) surface sites free for hydrogen transfer reactions. The next step is to see if we can facilitate reactions related to LTS, such as ethanol steam reforming (ESR), as ethanol is an important carrier of hydrogen (H₂).
2. Ethanol steam reforming (ESR) was investigated on unpromoted and potassium promoted (0, 0.85, 1.7, 2.6, 3.4, 4.3 and 8.5 wt.%) Pt/ZrO₂. Potassium doped Pt/ZrO₂ catalyst was compared to undoped Pt/ZrO₂ catalyst by utilizing the TPR profiles and EXAFS Fittings to determine the potassium loading and Pt size that result in the greatest hydrogen selectivity.

Methodology

DRIFTS and TPD of ethanol were used to probe the activity of the catalysts. First, ethanol adsorbs as the Type II ethoxy species, which is then converted to acetate by oxidative dehydrogenation. At lower temperatures, acetate decomposes in the desired forward direction to carbon monoxide, carbon dioxide and methane. At higher temperatures, the metal surface is expected to intercept the methane precursor (CH₃- and H-) for further steam reforming; or, the products can be fed to a downstream methane steam reformer. An analogous mechanism occurs in methanol steam reforming (MSR), where formate is an intermediate species rather than acetate as shown in the scheme below.

Results

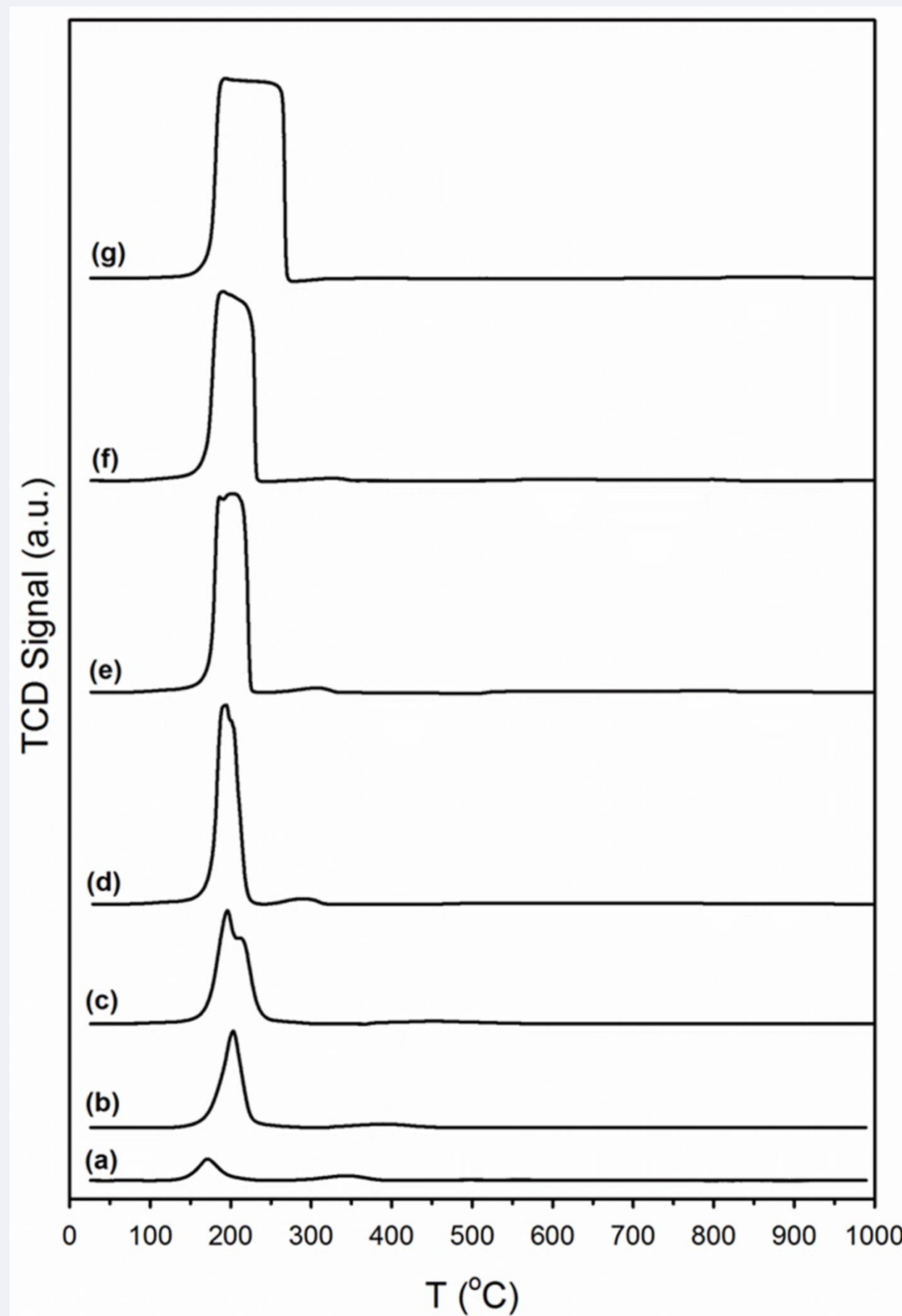


Figure 1: TPR profiles of (a) 2%Pt/ZrO₂, (b) 0.85%K-2%Pt/ZrO₂, (c) 1.7%K-2%Pt/ZrO₂, (d) 2.6%K-2%Pt/ZrO₂, (e) 3.4%K-2%Pt/ZrO₂, (f) 4.25%K-2%Pt/ZrO₂, and (g) 8.5%K-2%Pt/ZrO₂.

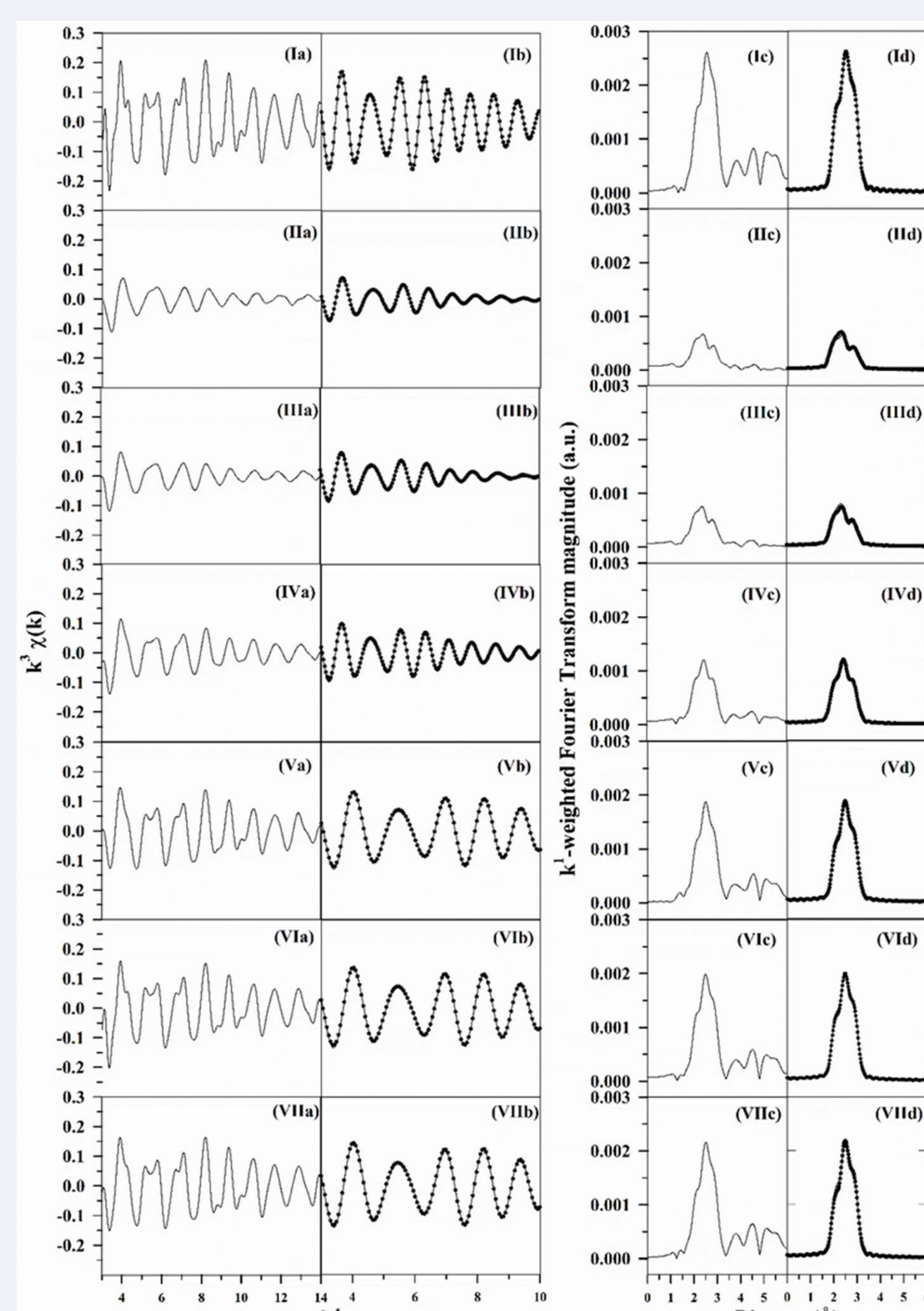


Figure 2: EXAFS fittings, including (a) raw k₁-weighted c(k) data, (b) (solid line) filtered k₁-weighted c(k) data and (filled circles) results of the fittings, (c) raw and (d) filtered k₁-weighted Fourier transform magnitude (solid line) data and (filled circles) results of the fittings for (I) PtO foil, (II) 2%Pt/m-ZrO₂, and 2%Pt/m-ZrO₂ with (III) 0.85%K, (IV) 1.7%K, (V) 2.6%K, (VI) 3.4%K, and (VII) 4.25%K.

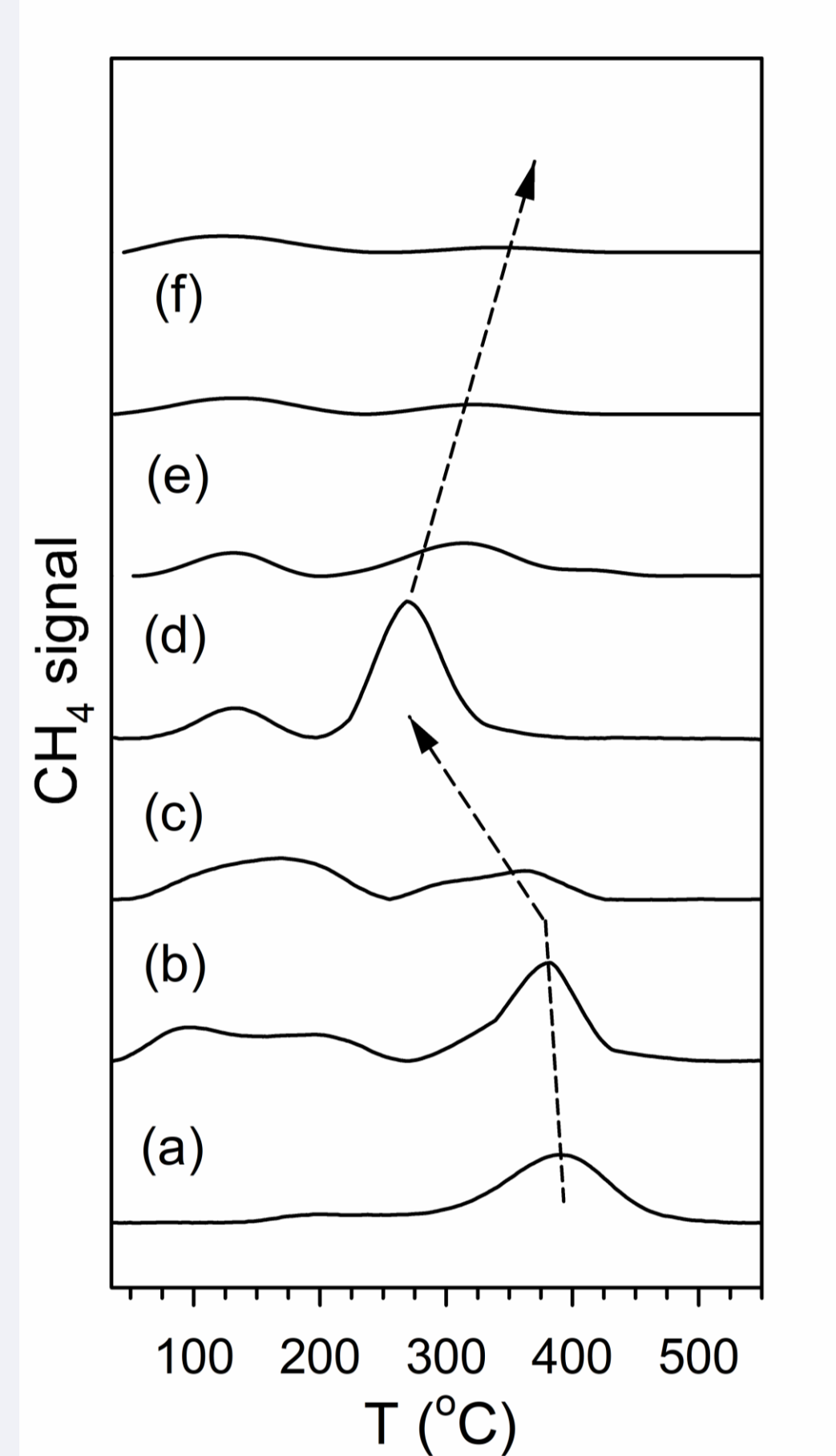
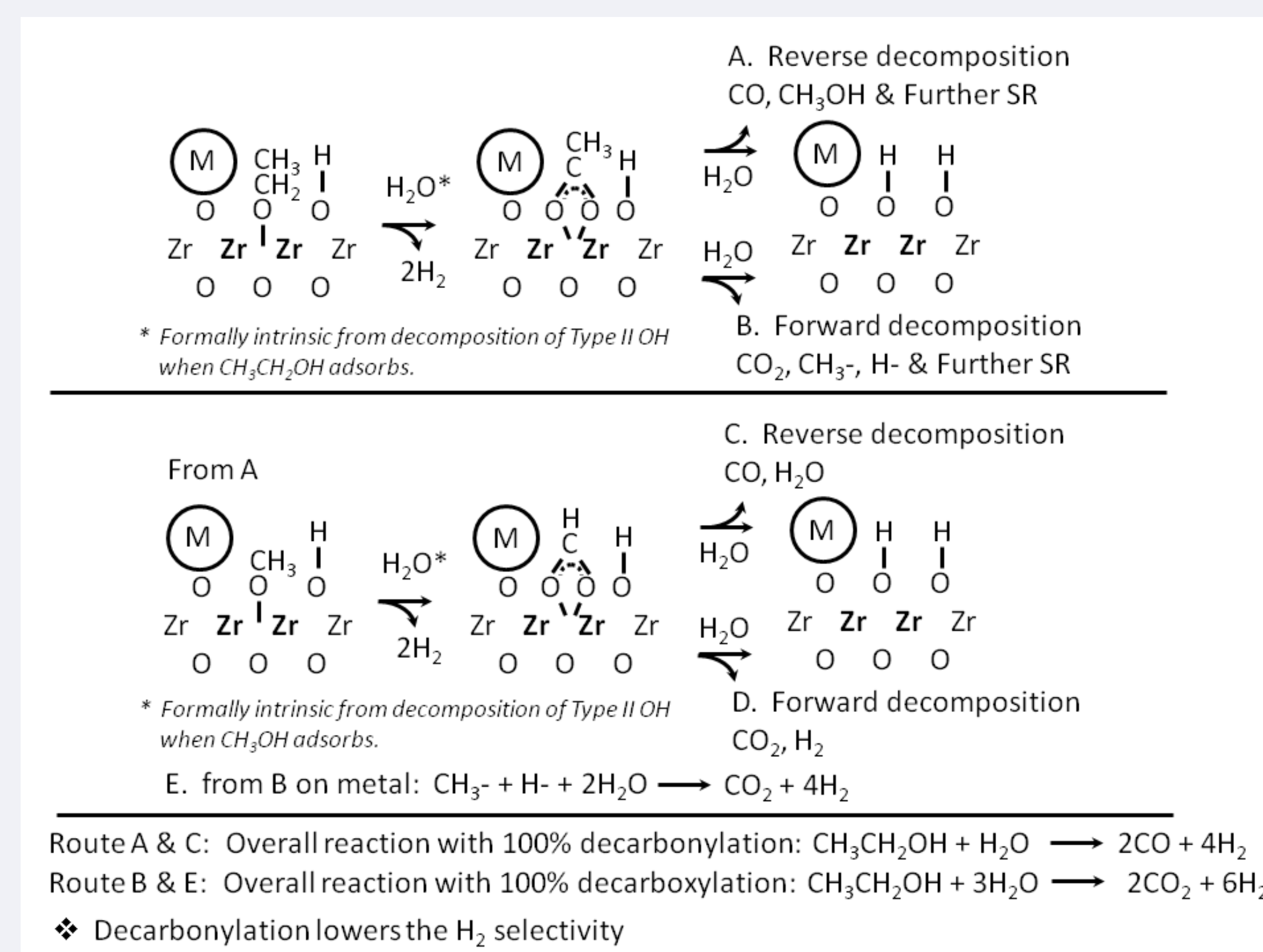


Figure 3: Methane signal during TPD for (a) 2%Pt/ZrO₂, (b) 0.85%K-2%Pt/ZrO₂, (c) 1.7%K-2%Pt/ZrO₂, (d) 2.6%K-2%Pt/ZrO₂, (e) 3.4%K-2%Pt/ZrO₂, (f) 4.25%K-2%Pt/ZrO₂, and (g) 8.5%K-2%Pt/ZrO₂.



Scheme 1: Routes for ethanol steam reforming

Skills and Experience

In this research project, catalysts were investigated using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), Temperature Programmed Reduction (TPR), Extended X-ray Absorption Fine Structure (EXAFS), and Temperature Programmed reaction (TP-Rxn) in order to assess the strength of the acetate C-C bond significant to the catalytic cycle of ESR. Also, communication and time management played a major role during the period of these experiments and analysis.

Future Plans

I plan to do research in the area of heterogeneous catalysis for energy applications when working in the petroleum refineries. Before that happens, I would like to go to graduate school and use this knowledge along with the experience learned working with Dr. Jacobs to improve the energy industry for a brighter and cleaner future.

What I Learned

In this experience, I learned that biomass is renewable, and the process of converting ethanol derived from biomass to hydrogen for use in fuel cells may provide a way to reduce greenhouse gas emissions such as carbon dioxide. In this project, it was found that the promoted catalyst cleaved the C-C bond at lower temperatures than the unpromoted catalyst, and thus showed that the promoted catalyst potentially improves the ESR reaction rates. This indicates that the alkali dopant weakens the C-C bond of acetate, which accelerates the rate determining step. Furthermore, when looking at the varying potassium loading for 2% Pt/ZrO₂, we found it to most optimal at 2.6 wt.%.

Acknowledgments

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Reference

1. Martinelli, M., Watson, C.D., Jacobs, G., “Sodium doping of Pt/m-ZrO₂ promotes C-C scission and decarboxylation during ethanol steam reforming,” International Journal of Hydrogen Energy, available online, 2019.