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Research Area

Heterogeneous catalysis is the study of accelerating multi-phase chemical mechanisms via the modification of activation energy barriers. The ultimate objective of this field of chemical engineering is to accelerate the rate of a chemical process occurring at a catalytic site while increasing efficiency and selectivity to desired products via careful analysis of chemical interactions between a catalyst and reacting species. At UTSA, the heterogeneous catalysis group applies these principles to optimize hydrogen production mechanisms. In the current contribution, the aim is to optimize catalysts for ethanol steam reforming for use in energy and fuel production.

Background

As the global population continues to grow exponentially, non-pollutant means of energy production are necessary to meet increasing energy demands while combating the depletion of fossil fuels. Hydrogen gas is of particular importance as it possesses the highest energy per unit mass of common fuels and can be generated from renewable resources. However, due to its low energy per unit volume, one potential solution is to store hydrogen in liquid chemical hydrogen carriers (e.g., light alcohols). As such, ethanol steam reforming (ESR; $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$) is commonly applied to produce hydrogen gas from renewable bioethanol. Bioethanol can be produced from fermentation, but as this competes with food, bioethanol from cellulose is a method currently being developed. ESR, however, is limited by the reverse decomposition of acetate in the intermediate which produces carbon monoxide (CO), and which ultimately decreases the overall hydrogen selectivity of the process. In this work, research has been conducted examining the possible promoting effect of lithium as a potential alkali promoter. The aim of the work was to accelerate the forward decomposition of the acetate intermediate into CO₂ and increase the overall selectivity to H₂. Acetate decomposition also produces CH₄, which can be further steam reformed by commercial catalysts (e.g., Ni-based); or catalysts may be designed in future to capture the methane (adsorbed CH₃- & H-) precursor for subsequent reforming. Ultimately, this study aims to improve the H₂ selectivity of the overall process by promoting the forward decomposition of acetate via the decarboxylation / demethanation route (ultimately generating 2CO₂ and 3H₂) versus the undesired reverse decomposition of acetate pathway via decarbonylation (generating 2CO + 2H₂). Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) and temperature programmed reaction of adsorbed ethanol/water was performed to determine whether Li⁺ addition electronically weakens the C-C bond in the acetate intermediate, thereby facilitating C-C scission of acetate and promoting forward acetate decomposition.

Objectives

- Examine the effects of catalytic lithium promotion for ethanol steam reforming.
- Determine the optimal loading of lithium for ESR.
- Ascertain the impact of lithium loading on the catalyst surface (e.g., support and Pt nanoparticle surfaces).
- Discover the underlying mechanism for lithium promoted ESR.
- Investigate the electronic effect of lithium on the intermediate acetate C-C bond.

Results

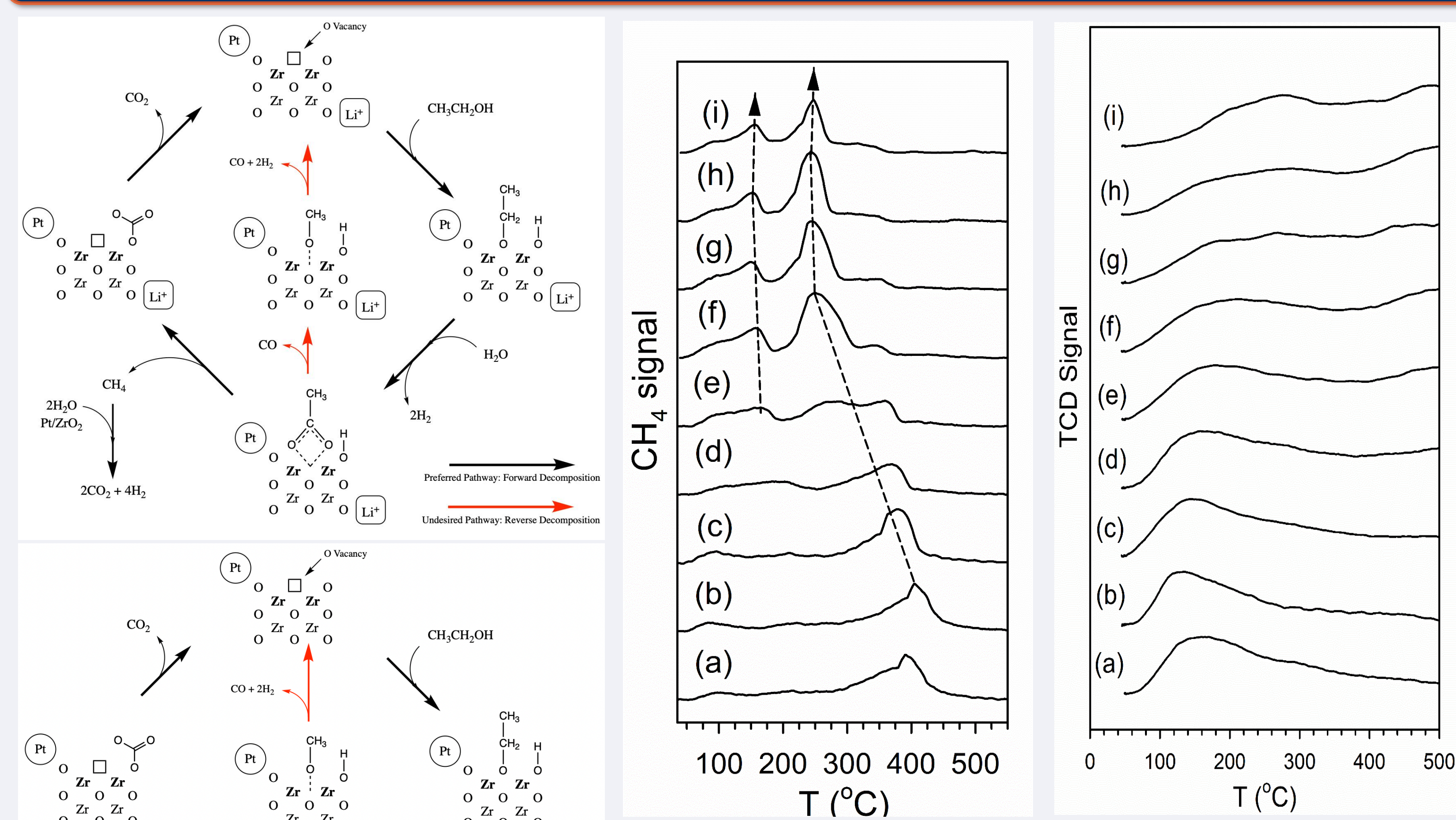


Figure 1: Simplified ethanol steam reforming mechanism using an activated Pt/ZrO₂ catalytic surface. (Top) Li promoted; (Bottom) Unpromoted

Figure 2: TPD-MS of adsorbed CO₂ over (a) 2%Pt/ZrO₂, (b) 0.15%Li-2%Pt/ZrO₂, (c) 0.30%Li-2%Pt/ZrO₂, (d) 0.54%Li-2%Pt/ZrO₂, (e) 0.75%Li-2%Pt/ZrO₂, (f) 1%Li-2%Pt/ZrO₂, (g) 1.25%Li-2%Pt/ZrO₂, (h) 1.5%Li-2%Pt/ZrO₂, and (i) 2%Li-2%Pt/ZrO₂.

Figure 3: TPD-MS of adsorbed CO₂ over (a) 2%Pt/ZrO₂, (b) 0.15%Li-2%Pt/ZrO₂, (c) 0.30%Li-2%Pt/ZrO₂, (d) 0.54%Li-2%Pt/ZrO₂, (e) 0.75%Li-2%Pt/ZrO₂, (f) 1%Li-2%Pt/ZrO₂, (g) 1.25%Li-2%Pt/ZrO₂, (h) 1.5%Li-2%Pt/ZrO₂, and (i) 2%Li-2%Pt/ZrO₂.

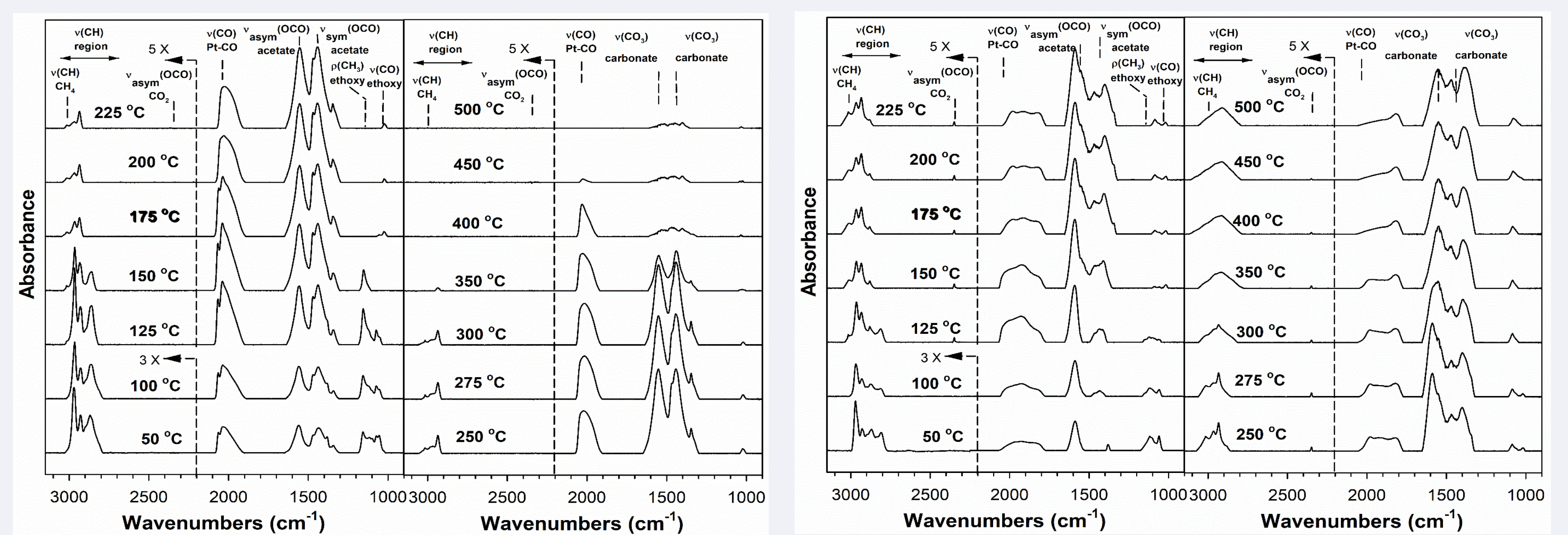


Figure 4: Comparison of the DRIFTS analysis of unpromoted 2%Pt/ZrO₂ (left) and the optimal loading at 1.0 wt.% Li from 50-500°C (right).

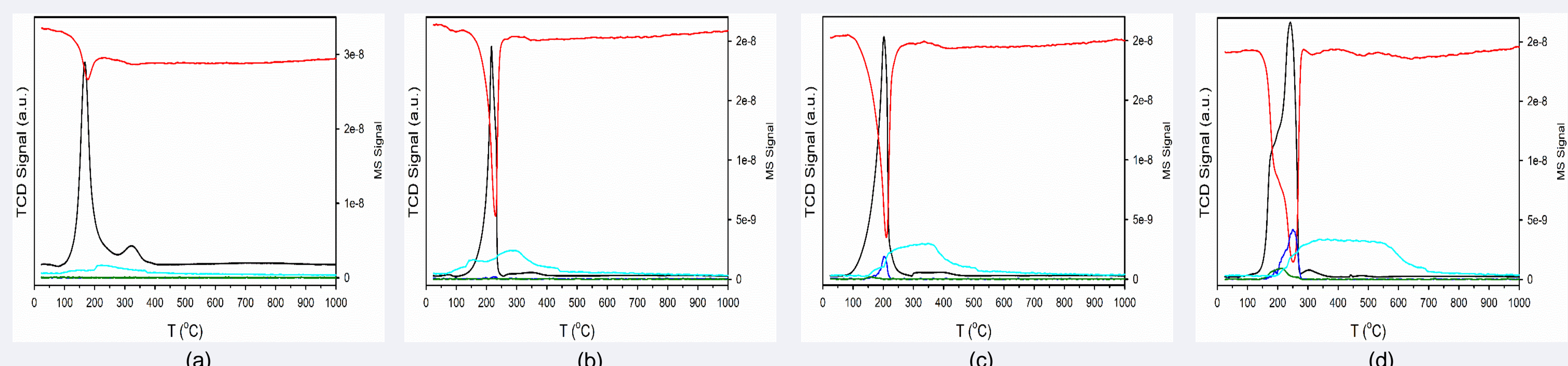


Figure 5: H₂-TPR (black) and TPR-MS profiles for (a) 2%Pt/m-ZrO₂ and the same catalyst with (b) 0.30%Li, (c) 0.75%Li, and (d) 1.5%Li, including MS signals for (red) H₂, (cyan) H₂O, (dark green) CO₂, and (blue) CO.

Figure 1 shows the associative mechanism for ethanol steam reforming supported on a Pt/ZrO₂ catalyst. The addition of lithium weakens the acetate C-C bond, allowing the reaction to proceed more by decarboxylation rather than decarbonylation, resulting in increased selectivity to H₂. DRIFTS results, shown in Figure 4, demonstrate that the optimal lithium loading (1.0 wt.%) shifted the CH₄ signal to lower temperatures, indicating a weakening of the acetate intermediate C-C bond and ultimately increasing the probability of proceeding through the favorable acetate decarboxylation / demethanation pathway. Due to the weakening of this bond, the reaction can proceed more rapidly. This is confirmed with greater confidence in Figure 2 by TPD-MS data showing that methane evolves at lower temperature with higher Li⁺ loadings. At loadings exceeding the optimum, the catalyst surface becomes overcrowded by Li⁺ resulting in a decrease in the rate of acetate decomposition due to site blocking (e.g., Pt). Platinum is known to facilitate decomposition of the third intermediate, carbonate, and it also acts as a porthole for hydrogen removal. Thus, excessive site blocking will lead to inhibition of CO₂ product removal, as seen in Figure 3. Moreover, CO₂ is an acidic molecule, and as lithium is basic in chemical nature, excessive Li⁺ loadings will also tend to inhibit CO₂ desorption. Figure 5 shows H₂-temperature programmed reduction profiles. The presence of Li⁺ tends to inhibit catalyst activation (H₂ uptake and H₂O/CO_x decomposition product evolution temperatures shift to higher temperatures with increasing Li⁺ content). Catalyst activation involves Pt oxide reduction, the generation of reduced defects in the zirconia, and the decomposition of surface carbonates.

Future Plans

The current catalysts will be tested using a fixed bed catalytic reactor. In the future, our group will continue to test the alkali series (type and loading) as promoters of Pt/zirconia catalysts for use in converting liquid chemicals carriers (e.g., ethanol, methanol, formaldehyde, etc.) to hydrogen. We are interested in determining the effect of alkali size and basicity in this chemical promotion. Upon completion, we expect to publish a comprehensive summary on the effect of alkali dopants.

What I Learned

I discovered that 1.0 wt.% is the likely optimal lithium loading for the tested Pt/zirconia catalysts used for ethanol steam reforming. At this loading, the forward acetate decomposition reaction proceeds more quickly through the favored decarboxylation / demethanation pathway. DRIFTS and TPD-MS demonstrate that lithium clearly facilitates the C-C scission of acetate in ESR, which should improve the H₂ selectivity of the overall ethanol steam reforming process.

Skills and Experience

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

Acknowledgements

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References

Michela Martinelli, Jonathan D. Castro, Nour Alhraki, Maria E. Matamoros, A. Jeremy Kropf, Donald C. Cronauer, Gary Jacobs, "Effect of sodium loading on Pt/ZrO₂ during ethanol steam reforming," Applied Catalysis A: General 610 (2021) 17 pp. <https://doi.org/10.1016/j.apcata.2020.117947>