Using Catalysts with Partially Reducible Oxides (PRO) to Facilitate the Reverse Water-Gas-Shift Reaction in CO_2 Hydrogenation

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Heterogenous Catalysis Lab

For this experiment, the heterogenous catalysis lab compared the activity of solid catalysts with supports made using partially reducible oxides (PRO) and non-partially reducible oxides in the presence of carbon dioxide (CO_2) and hydrogen gas (H_2). This was done to understand if catalysts with PRO support were more active than catalysts with non-PRO support during reverse-water-gas-shift (RWGS), an important first step in the pathway toward producing hydrocarbons utilizing CO_2. The catalysts being investigated are: $RuCuZrO_2$, $RuAl_2O_3$, $RuZrO_2$, $RuMgO$, and $RuTiO_2$. Results for $RuCuZrO_2$ and $RuAl_2O_3$ are discussed below.

Background

Catalysts lower the activation energy of a reaction by providing an alternative pathway, and with heterogeneous catalysts, this involves reactions on catalyst surfaces. This project studied and compared catalysts with PRO supports and non-PRO supports that are used to support ruthenium nanoparticles for the formation of hydrocarbons through CO_2 hydrogenation pathways involving RWGS and CO hydrogenation (e.g., methanation and eventually, Fischer-Tropsch synthesis). This project studied the reverse water-gas-shift reaction (RWGS) mechanism to see if catalysts with PRO support increased surface activity via a formate mechanism taking place at the Ru/PRO interface; this is followed by normal CO hydrogenation on Fischer-Tropsch active metals, such as ruthenium. Formate is a key intermediate in forward and reverse water-gas shift reactions. The product CO is then hydrogenated to methane under our ambient pressure conditions. In the future, however, our aim is to apply the catalysts at higher pressures to produce longer hydrocarbon chains via the Fischer-Tropsch synthesis (FTS) reaction. Useful products like diesel fuel, jet fuel, lubricants, and other organic products are the result of these longer hydrocarbon chains. While FTS using syngas (CO + H_2) is a commercial process, the hydrogenation of CO_2 requires significant catalyst development.

Objectives

- Perform IR scans at different temperatures for the selected catalysts and collect data
- Process the scanned IR data and combine all temperature sets for each catalyst
- Study and compare the behavior of catalysts with and without PRO support related to the formation of formate and methane via RWGS (i.e., converting CO_2 to CO) and subsequent CO hydrogenation.

Methodology

- Each catalyst was scanned with a Fourier transform Infrared Spectrometer (FTIR) in the presence of CO_2 and H_2 between a temperature range of 50-400 ℃
- Each scan was processed and baseline corrected.
- The data set for every temperature was combined into one single excel file for each catalyst.
- Data for each catalyst was plotted in a stacked format to analyze the activity at wavelength ranges specific to formate ($2800-2850cm^{-1}$, $\sim1580cm^{-1}$, $1300-1350cm^{-1}$), methane ($\sim3010\ cm^{-1}$) and water ($3750cm^{-1}$, $1640cm^{-1}$)
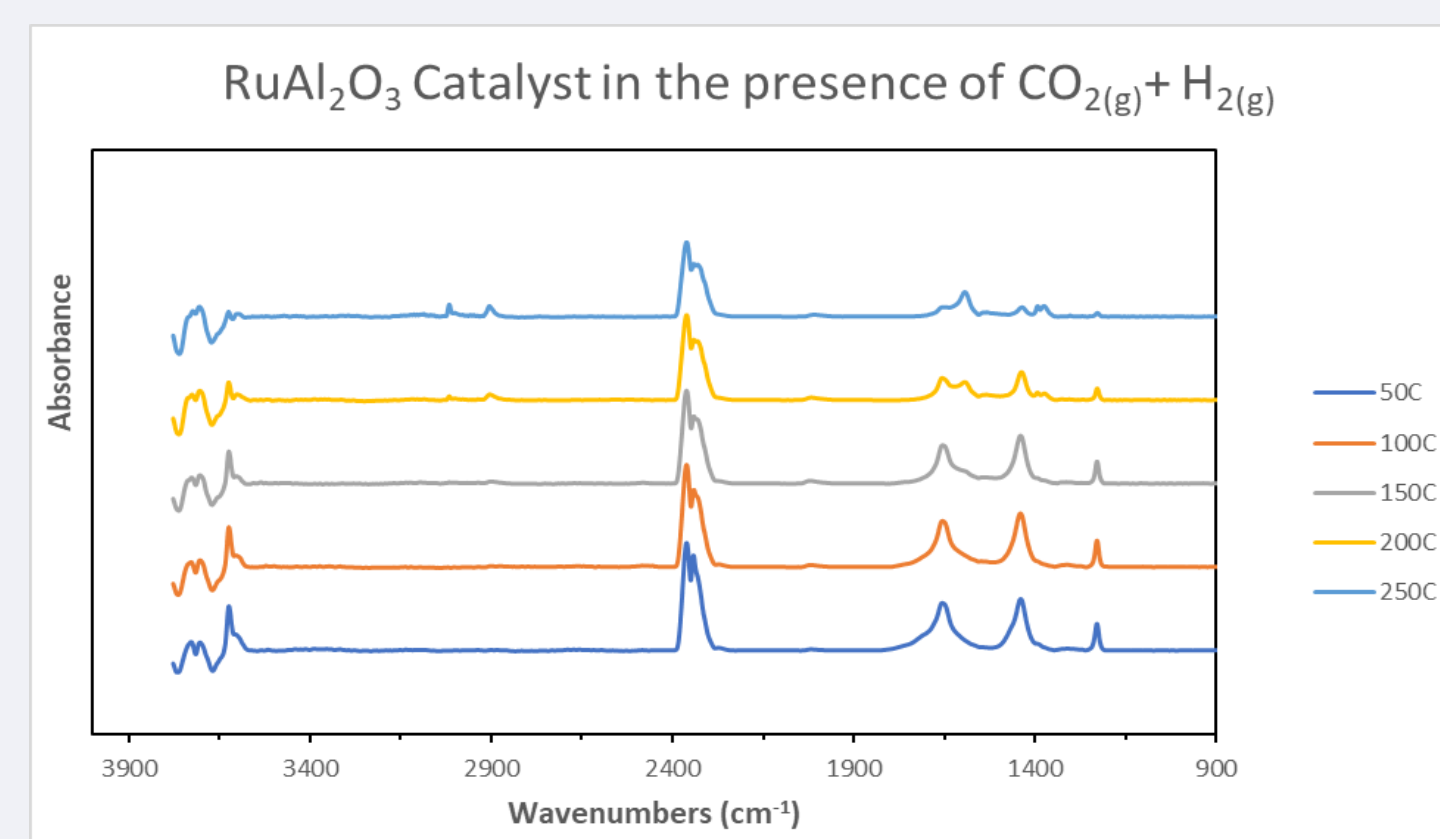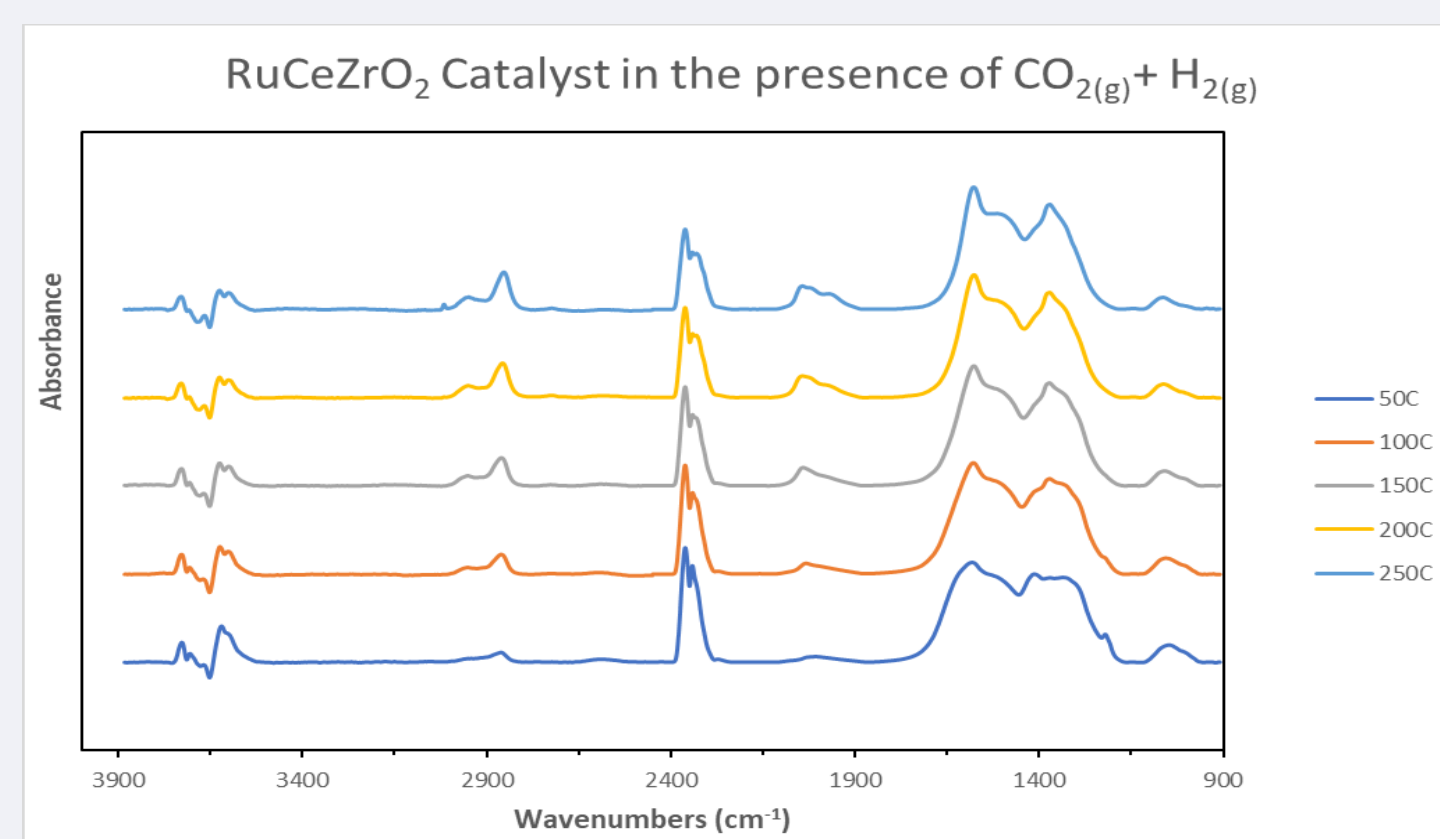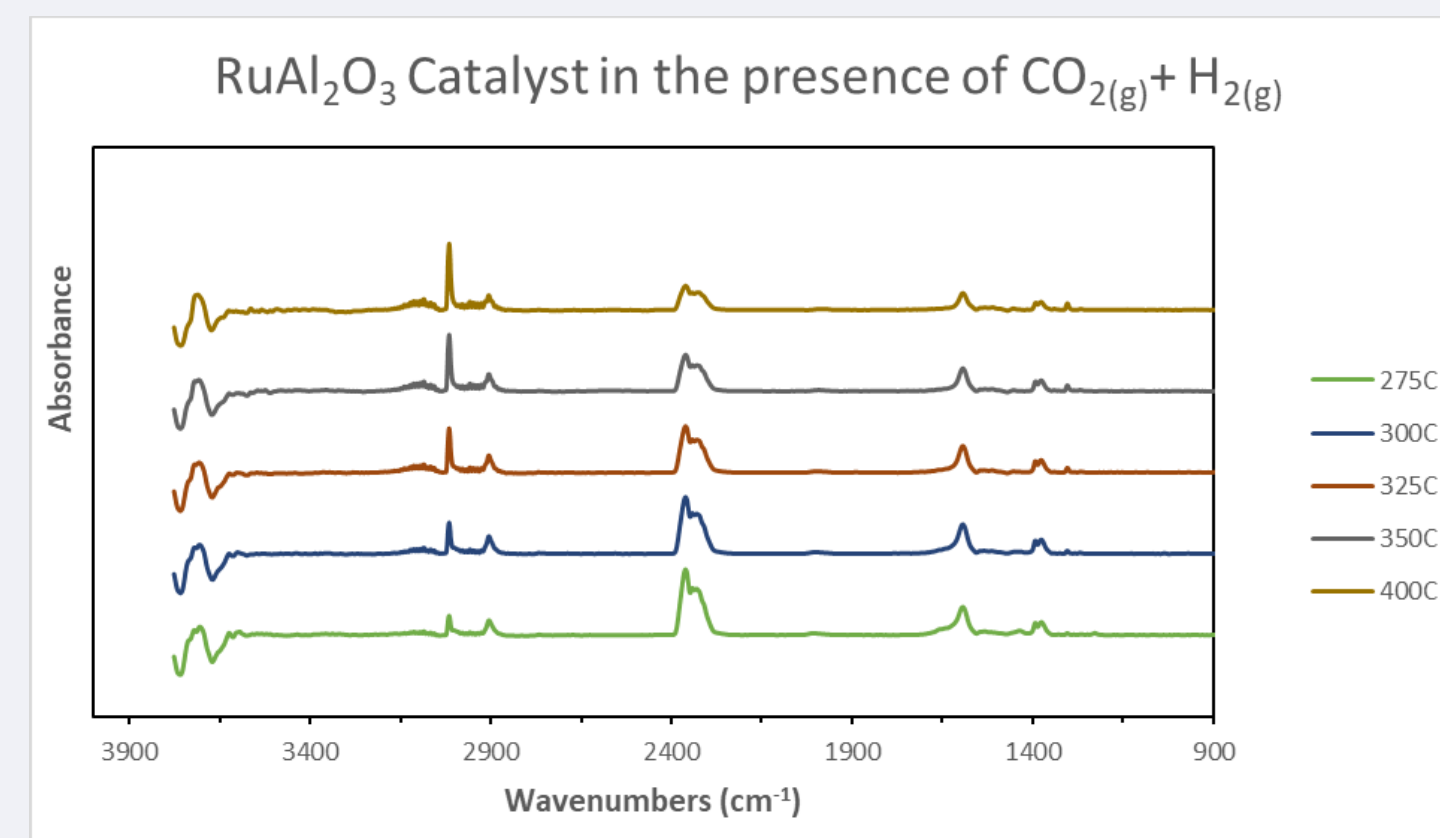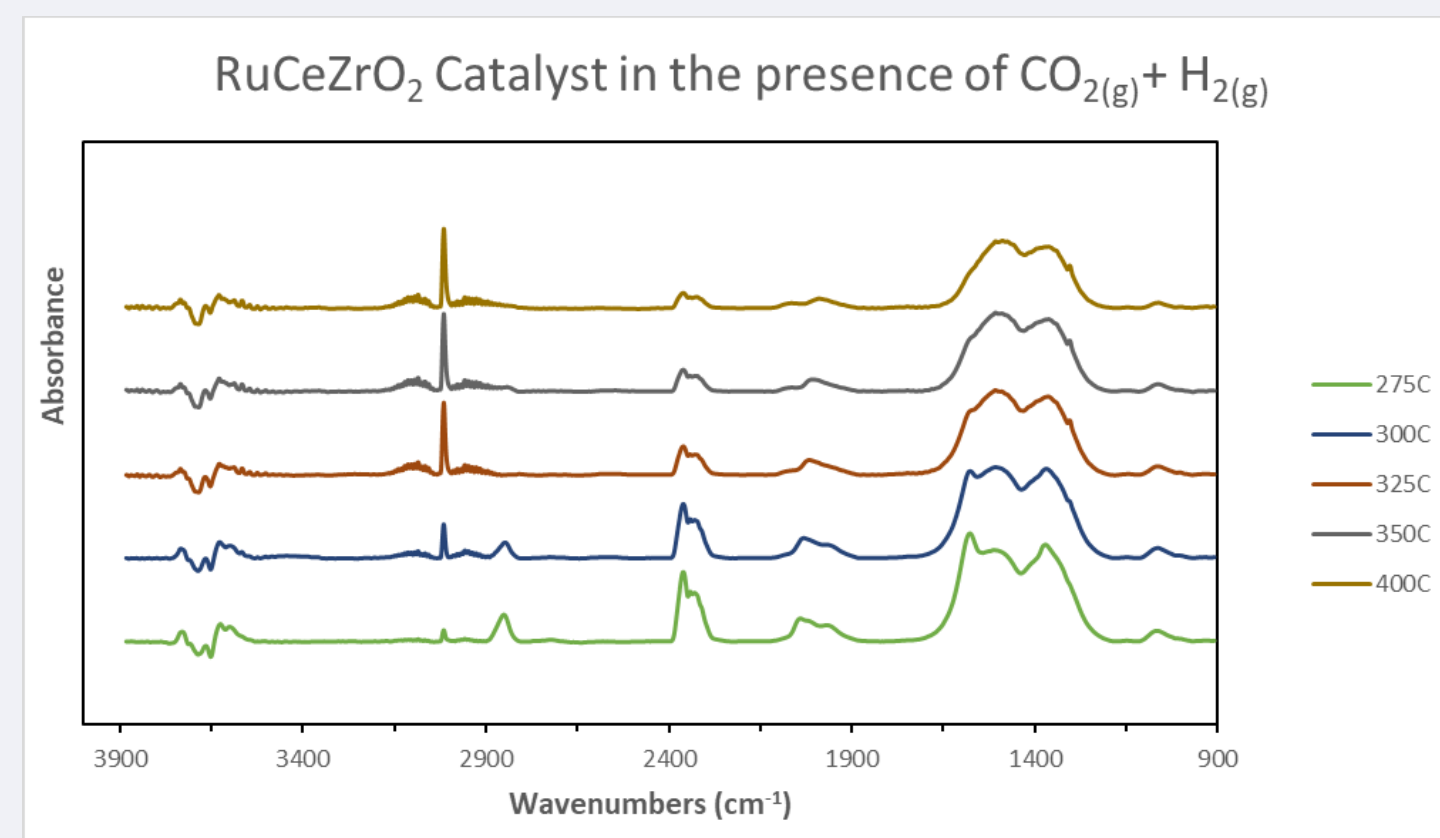
Results

The $RuCeZrO_2$ is a catalyst with a PRO support and $RuAl_2O_3$ is a catalyst with non-PRO support. In this project RWGS was studied. For both catalysts, IR signals for the formate C-H stretching, asymmetric and symmetric carbonyl (C=O) stretching were observed at $2800-2850\ cm^{-1}$, $\sim1580\ cm^{-1}$, and $1300-1350cm^{-1}$ respectively. The IR signal for methane C-H stretching was observed at $\sim3010\ cm^{-1}$. OH stretch and bending behavior for water was observed at $\sim3750\ cm^{-1}$ and $1640\ cm^{-1}$ respectively. The reagent carbon dioxide (CO_2) has C=O stretching at $\sim2350cm^{-1}$. A summary of the activity for each molecule based on the intensity of their functional groups are compared for each catalyst below.

Catalyst	Formate	Methane	Water	CO_2
$RuCeZrO_2$	Increases in intensity as a strong and broad signal between 50-250°C. Decrease as temperature increases between 275-325°C (whereas methane rises). This is consistent with an intermediate.	Signal detected as a separate species from formate C-H stretching by 250°C. Increases in intensity to an intense band by 325°C, leveling off above that. It is more intense than the signal for Ru/Al_2O_3, as expected.	Medium throughout entire temperature range	Strong between 50-250°C and decreases as temperature increases between 275-400°C.
$RuAl_2O_3$	Weak signal that is detected at 150°C and increases slightly up to 325°C, leveling off or slightly decreasing above this temperature.	Detected at 200°C and slowly increases with temperature. The signal at 325°C+ is much weaker than that of $RuCeZrO_2$.	Medium and broad.	Strong between 50-250°C and then slightly decreases until 325°C.

Skills and Experience

- Basic understanding of setting up experimental system with tubing, flow meters, directional valves, and switches.
- Learning about the different types of catalysts.
- Performing FTIR scans and adjusting temperature.
- Interpreting Fourier-transform infrared spectroscopy (FTIR) and processing data using Omnic software.
- Processing and plotting data using Excel.

What I Learned

Using catalysts containing an active PRO support increased methane production by facilitating production of the CO intermediate via the RWGS reaction. Formate signals, indicative of the proposed RWGS surface intermediate, were significantly stronger using catalysts containing the PRO. Performing CO_2 hydrogenation through RWGS and methanation gives us insight into the mechanism. This provides insights that will guide us into future work aimed at producing larger hydrocarbons through CO_2 hydrogenation by way of Fischer Tropsch synthesis at higher pressure.

Future Plans

We have been invited to submit our research for a special issue of Chemical Engineering Science which requires preparing a report over the summer. This will focus on the results above and those not included in this presentation.
I will perform a new research project over the summer with my current mentor.

Acknowledgments

References

- "IR Spectrum Table & Chart." *Millipore Sigma*, www.sigmaaldrich.com/technical-documents/articles/biology/ir-spectrum-table.html