CO_2 Hydrogenation: Comparing Ru catalysts with partially reducible oxide supports to non-partially reducible oxides in reverse water-gas-shift (RWGS)

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Heterogeneous Catalysis Lab

Name: *Martin Isai Ayala*
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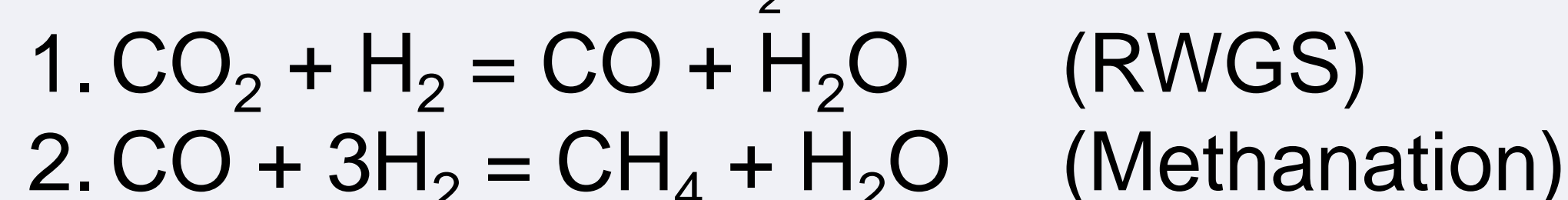Primary Investigator: *Dr. Gary Jacobs*

The Heterogenous Catalysis Lab is directed by Dr. Gary Jacobs. Dr. Jacobs has directed his research for 20 years to the development, characterization, and testing of novel catalysts used for many applications like syngas conversion and hydrogen production and purification.
This project investigated ruthenium (Ru) catalysts with partially reducible oxide supports (PRO) and non-partially reducible oxides to produce hydrocarbons $[CH_2]_n$ via reverse water gas shift and CO hydrogenation. The catalysts under investigation were Ru-Cu/ZrO_2, Ru/Al_2O_3, Ru/ZrO_2, Ru/MgO, and Ru/TiO_2. Results for Ru/CeO_2, Ru/ZrO_2, Ru/Al_2O_3 are discussed below.
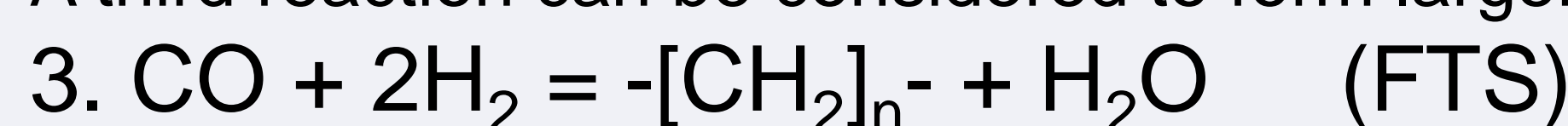
Motivation or Background

CO_2 methanation is a promising solution to reduce the increased CO_2 emissions that contribute to the greenhouse effect and rising global temperatures (1). It is also a promising field of study due to existing pipeline infrastructure for transporting methane. This set of experiments seeks to show how catalysts with partially reducible oxide supports favor formate intermediates (important for RWGS) that further dissociates into CO; the CO is further hydrogenated by surface hydrogen into methane (CH_4). Further study into catalysts for CO_2 hydrogenation paves ways to find ways to use CO_2 as syngas for higher number carbon chains via Fischer Tropsch synthesis (FTS). Higher number carbon chain (C_{5+}) products include gasoline, diesel, jet fuel, oil, and alcohols.

Consider two reactions for CO_2 methanation:

1. $CO_2 + H_2 = CO + H_2O$ (RWGS)
2. $CO + 3H_2 = CH_4 + H_2O$ (Methanation)

A third reaction can be considered to form larger hydrocarbons:

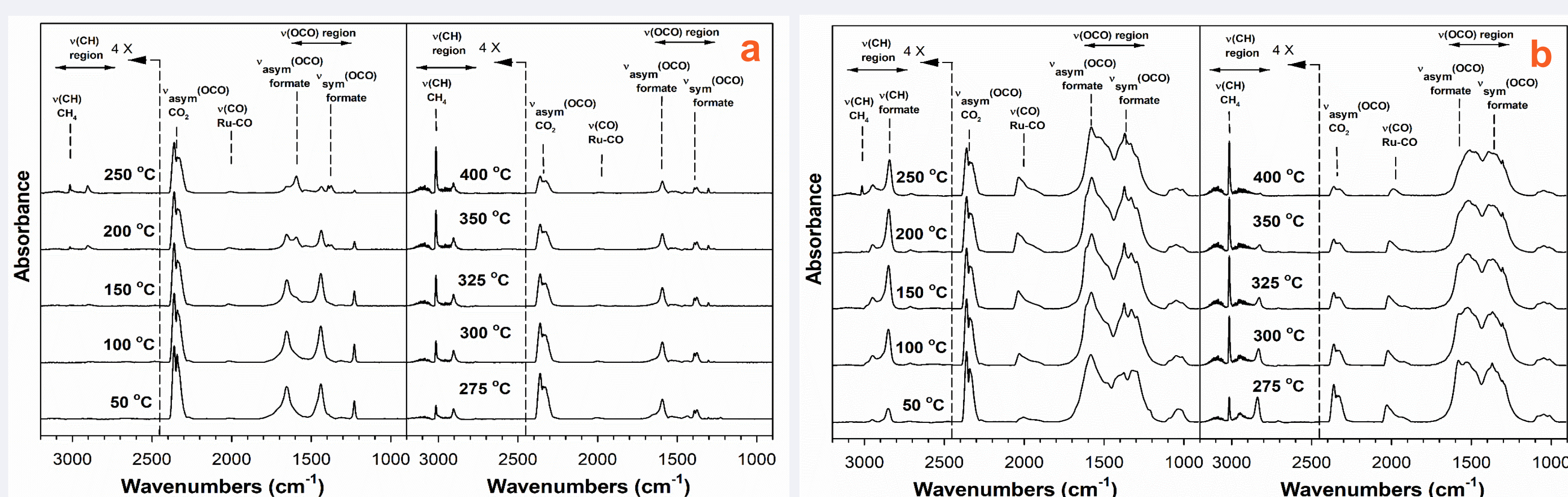3. $CO + 2H_2 = -[CH_2]_n- + H_2O$ (FTS)

Objectives

1. Determine the species adsorbed onto the catalyst surface, including carbonates (monodentate, bidentate, bridged, or polydentate), formate, carbonyls, and hydroxyl groups
2. Classify which catalysts possess reduced defect sites that can stabilize formates, which decompose into CO and active OH groups. The latter further form into H_2O, generating a vacancy. (PRO)
3. Compare non-PRO and PRO methane production from CO_{ad} hydrogenation.

Methodology

In situ experiments were studied using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Catalysts were studied under different conditions including a 4% CO_2 in He mixture flow, followed by a flow of 4% CO_2, 60% H_2 in He and a final temperature programmed desorption (TPD) of CO_2 was performed. For each experiment, scans were taken between 50-400°C. Catalysts were also reduced before each experiment under pure hydrogen at 500°C for 1h. Results for CO_2 & H_2 flow are displayed below. Scans were processed using Omnic software and then plotted with Excel.

Results

Experimental

Catalysts	CO_2 conversion (%)	Reaction Rate ($mol/mol_{met}s$)	CH_4 Selectivity (%)
1Ru/ZrO2	9	1.35	97.29
5Ru/ZrO2	8.7	0.31	96.46
Ni/ZrO2	8.1	0.06	97.5
5 Ru/Al2O3	-	0.06	-

1% Ru/ZrO_2 had the highest CH_4 activity with a reaction rate and selectivity of 1.35 s^{-1} and 97.3%. Compared to 5 Ru/Al_2O_3 reaction rates for 1% Ru and 5% Ru catalysts were larger by 23-fold and 5-fold, respectively.
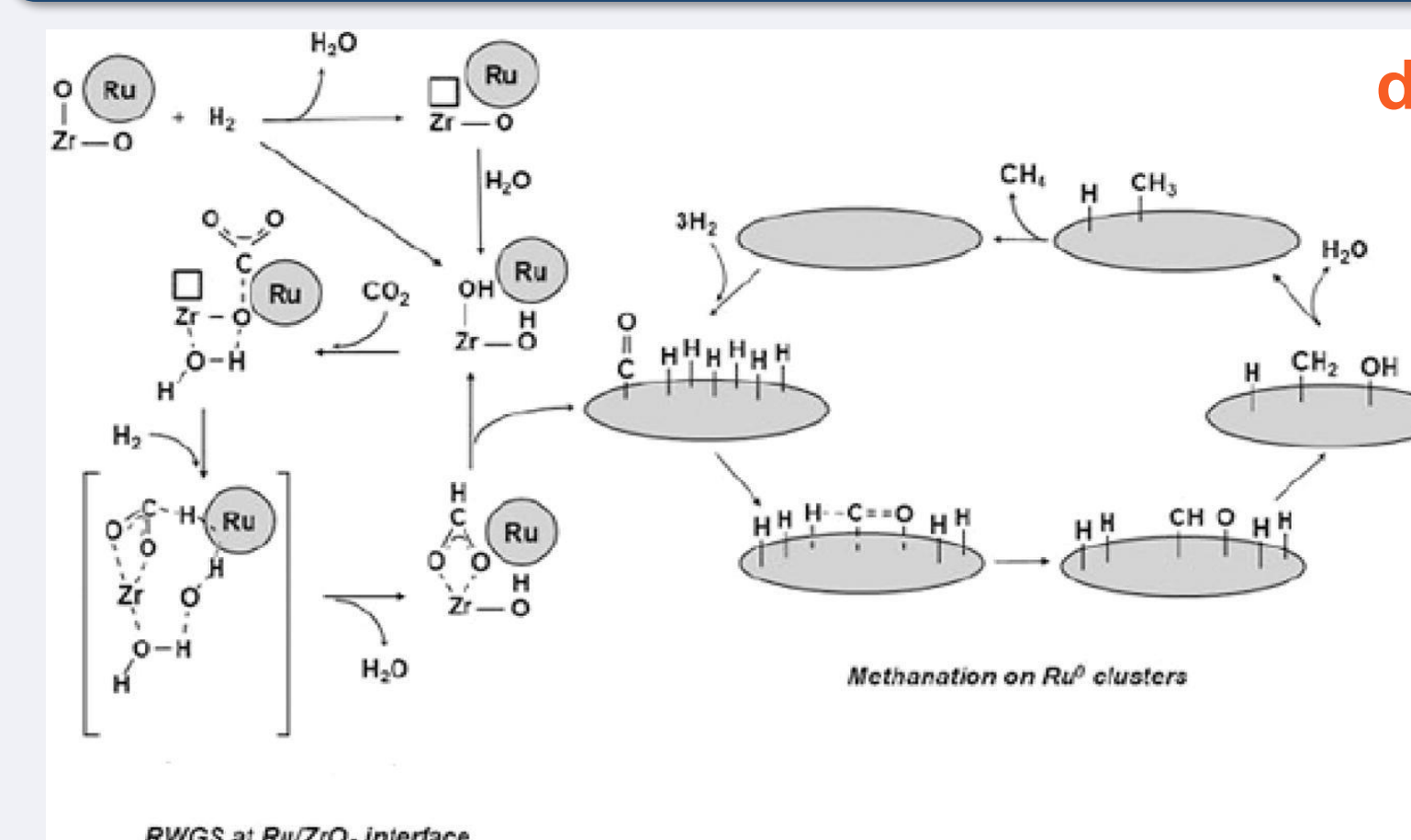

DRIFTS spectra collected under flowing CO_2 and H_2 and sequential heating for each catalyst.
(a) Ru/Al_2O_3 (b) Ru/CeO_2 (c) Ru/ZrO_2 (d) potential mechanism

Catalysts that have PRO supports (b-c) exhibit strong IR signals indicative of formate at ν(CH) 2800-2850 cm^{-1}, ν_a(OCO) ~1580 cm^{-1}, and ν_s(OCO) 1300-1350 cm^{-1}. These appear at T = 50 °C and diminish as temperature increases.
ν(OH) bending indicative of surface bound water can be observed in 1600-1640 cm^{-1} range (3).
Gas phase CO_2 is observed at ~2350 cm^{-1} (2). ν(CH) for methane is observed at 3010-3100 cm^{-1} (2).
Catalysts with PRO support (b-c) display strong methane activity and reduced formate bands. at T = 275 °C
Significant methane formation possibly from formate decomposition is noticed for Ru/CeO_2 and Ru/ZrO_2 at T = 300 °C and T = 275 °C respectively.
Ru/Al_2O_3 has significant methane formation at T = 350°C without significant formate decomposition. This indicates formate intermediacy is not favored.
Comparing reaction rates and selectivity we see that Ru/ZrO_2 and Ru/CeO_2 exhibit higher methane activity than Ru/Al_2O_3 overall and at lower temperatures.

Conclusion

Catalysts with partially reducible oxide supports contribute to activation of water and surface hydroxyls that contribute to increased formate production, a key intermediate in RWGS. Favoring RWGS also leads to increased hydrocarbon formation indicated by methane gas. Understanding CO_2 methanation guides us to develop catalysts that favor hydrogenation of CO_2 into larger carbons chains by Fischer Tropsch Synthesis.
Most active catalyst was Ru/ZrO_2 followed by Ru/CeO_2. This was due to the partially reduced oxide support favoring CO_2 decomposition into formate intermediates and CO_{ad} hydrogenation.

Skills and Experience

1. Applying infrared spectroscopy to the characterization of catalysts.
2. Organizing and streamlining vibrational modes of different adsorbed species for each catalyst.
3. Reading and summarizing research articles about related catalytic experiments.
4. Gained critical thinking skills by developing insight into working mechanism.

Future Plans

Further research to determine optimal doping levels on catalysts with FTS active metals (Ru, Co) and PRO supports (CeO_2, ZrO_2) for CO_2 hydrogenation is ongoing research. In addition, we are currently exploring the effect of chemical promoters on the reaction rate.

Acknowledgments

References

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3. Infrared Spectroscopic Study on the Surface Properties of γ-Gallium Oxide as Compared to Those of γ-Alumina, A. Vimont, J. C. Lavalley, A. Sahibed-Dine, C. Otero Areán, M. Rodríguez Delgado, and M. Daturi, The Journal of Physical Chemistry B 2005 109 (19), 9656-9664