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Research Area

What is Heterogenous Catalysis?

- Catalysts are used in industry to change the yield of a reaction by altering the activation energy. This includes lowering the activation energy of desired reactions and raising the activation energy of undesired pathways.
- The research can be applied to many fields including but not limited to energy delivery and storage.
- This can be used to increase a desired product or to reduce the selectivity of an undesired reaction pathway
- For heterogenous catalysis, the catalyst is usually present in the solid phase, whereas the reacting chemical species are in a fluid phase.

Background

Steam reforming processes are used to convert organic compounds to syngas (carbon monoxide and hydrogen). This is an important process in industries where hydrogen is produced, as well for the production of synthetic fuels and chemicals from the syngas. For the case of FSR, formaldehyde is a toxic compound used in manufacturing of resins, coatings, building materials, and as a preservative. The waste from these processes can be reformed to reduce the toxic waste and to use the formaldehyde as a chemical carrier of hydrogen (e.g., for use in fuel cell applications, etc.). Formaldehyde is also a proposed intermediate in the methanol steam reforming (MSR) reaction, which is also used to produce H₂. Therefore, investigating FSR is important for shedding light on the catalytic pathways occurring in MSR. For the FSR process, it is important to consider that various catalysts and alkali promoters can be used to alter selectivity (e.g., the relative rates of reactions occurring), and to optimize the selectivity of H₂. The purpose of this research was to shed light on the role of alkali promoters in altering selectivity and to provide insight into how alkali promoters influence the decomposition of the formate intermediate, which controls H₂ selectivity. This was accomplished by analyzing the isotope effect associated with formate decomposition.

Objectives

- Study the effects of different alkali promoters in FSR
- Explore the change in rate using an isotope effect
- Infer about the reaction mechanism involved in the formaldehyde steam reforming process by referencing data taken in multiple experiments and prior publications.
- Discuss future research directions based on the findings of this work.

Results

Figure 1

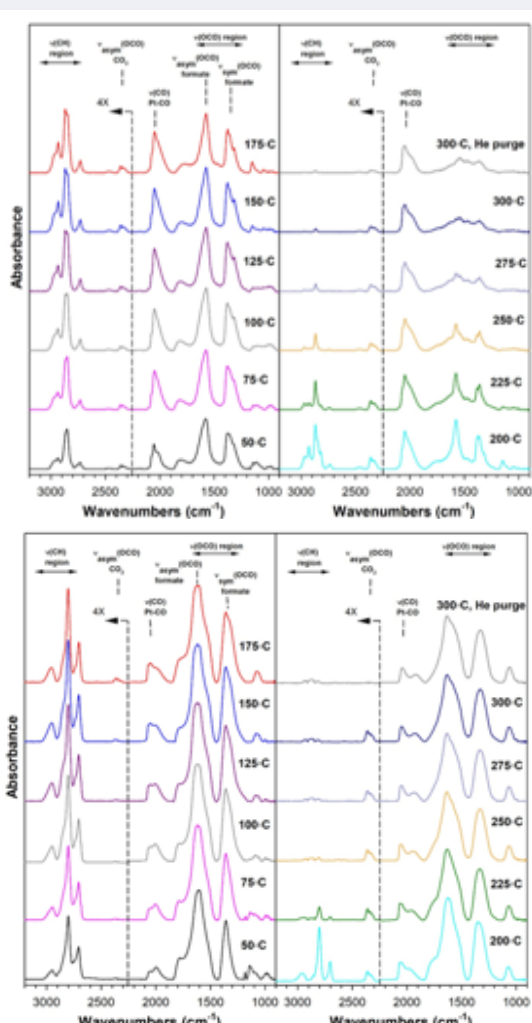


Figure 2

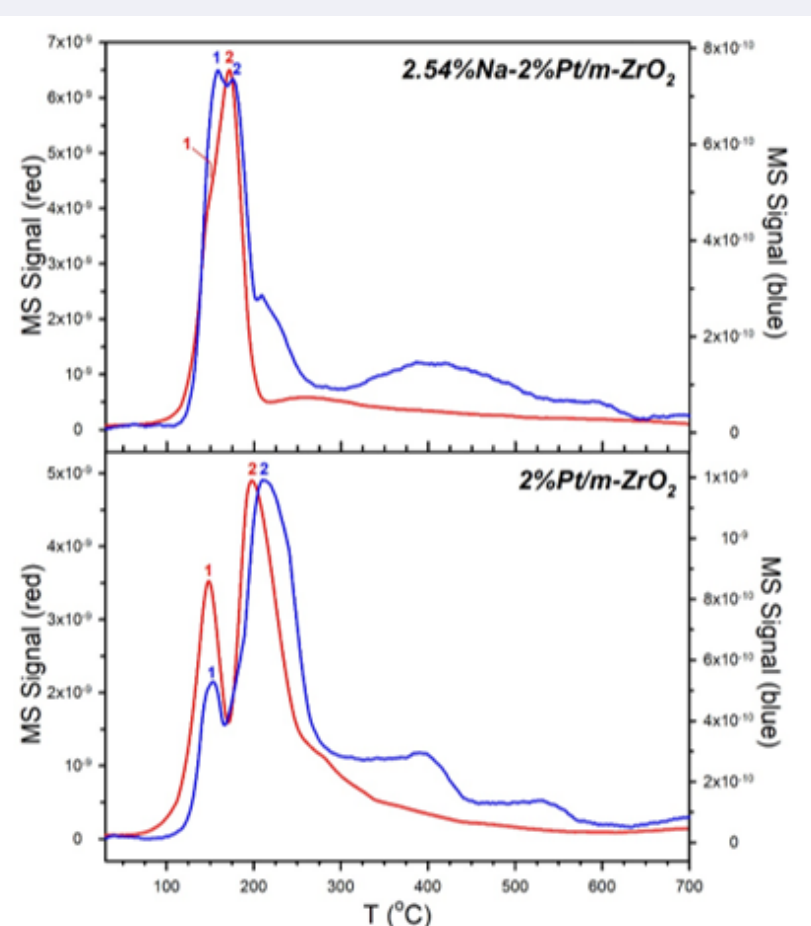
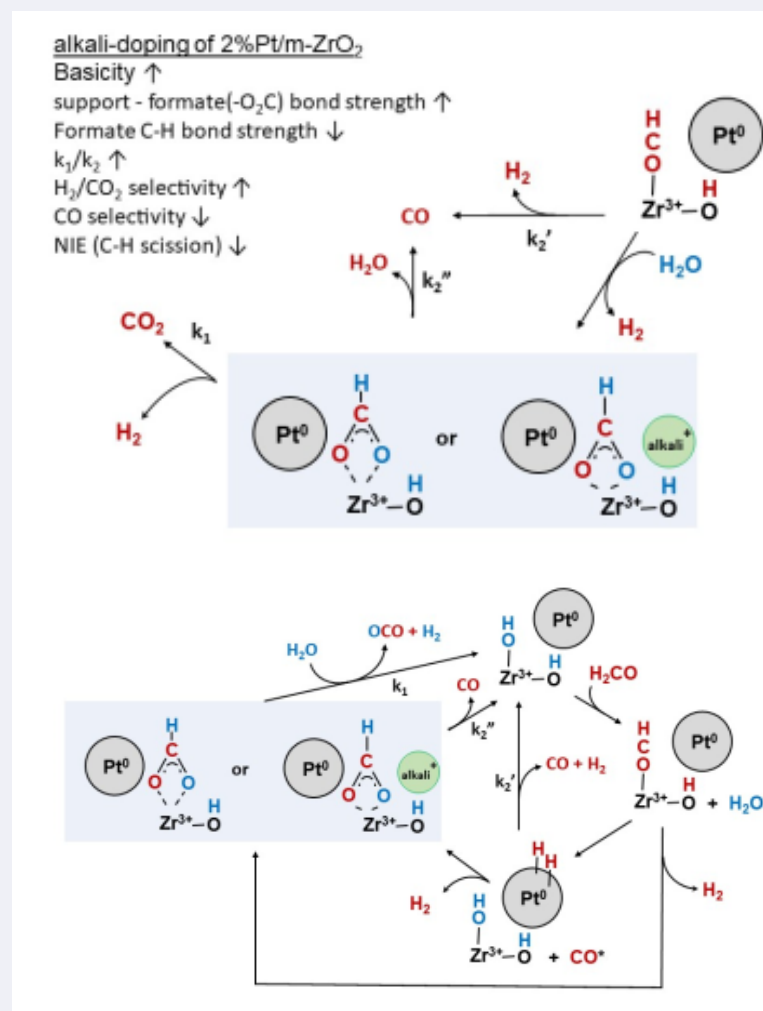


Figure 3



Tables

	H ₂ Step #1 (°C)	H ₂ Step #2 (°C)	CO (°C)	CO ₂ (°C)	% CO peak < 225°C area relative to 2%Pt/m-ZrO ₂	% CO peak < 225°C area relative to 2%Pt/m-ZrO ₂ deuterated
2%Pt/m-ZrO ₂	154	190	159	192	100.0	35.0%
0.75%Li-2%Pt/m-ZrO ₂	(< 167)	177	164	196	42.9	15.0%
1.8%Na-2%Pt/m-ZrO ₂	(< 155)	164	156	165	36.4	12.7%
2.54%Na-2%Pt/m-ZrO ₂	(< 150)	170	156	188	4.3	1.5%
2.55%K-2%Pt/m-ZrO ₂	(< 150)	160	151	161	8.6	3.0%
4.65%Rb-2%Pt/m-ZrO ₂	(< 150)	158	151	169	22.1	7.7%
5.78%Cs-2%Pt/m-ZrO ₂	(< 150)	155	159	170	16.8	5.9%

	D ₂ Step #1 (°C)	D ₂ Step #2 (°C)	CO ₂ (°C)	% CO peak < 225°C area relative to 2%Pt/m-ZrO ₂	
2%Pt/m-ZrO ₂	(< 165)	219	169	222	100.0
0.75%Li-2%Pt/m-ZrO ₂	(< 176)	210	181	238	38.1
1.8%Na-2%Pt/m-ZrO ₂	(< 175)	192	168	238	19.8
2.54%Na-2%Pt/m-ZrO ₂	(< 165)	172	163	220	4.2
2.55%K-2%Pt/m-ZrO ₂	(< 156)	169	159	178	24.4
4.65%Rb-2%Pt/m-ZrO ₂	(< 162)	171	164	192	20.7
5.78%Cs-2%Pt/m-ZrO ₂	(< 157)	165	160	179	9.9

	CH ₂ O conversion (%)	CO selectivity (%)	CO ₂ selectivity (%)
2%Pt/m-ZrO ₂	86.00	17.49	82.51
2.54%Na-2%Pt/m-ZrO ₂	89.78	-	100
0.75%Li-2%Pt/m-ZrO ₂	89.68	-	100

	H or D	T _{0.99%} (°C)	E _{0.99%} (kJ/mol)	ΔE _{0.99%} (kJ/mol)	NIE	(NIE with Na) / (NIE without Na)
2%Pt/m-ZrO ₂	H	199	134.4	2.9	2.4	0.67
	D	209	137.3			
2.54%Na-2%Pt/m-ZrO ₂	H	171	126.2	1.5	1.6	0.67
	D	176	127.7			

- Figure 1:** DRIFTS of 2%Pt/m-ZrO₂, including adsorption of 10% formaldehyde in H₂O following at 50°C helium purge and then adding 4.4% H₂O at 75°C, 100°C, 125°C, 150°C, 175°C, 200°C, 225°C, 250°C, 275°C, and 300°C, including a helium purge for 15 min at 300°C (top) and DRIFTS of 2.54%Na-2%Pt/m-ZrO₂, including adsorption of 10% formaldehyde in H₂O at 50°C following helium purge and then adding 4.4% H₂O at 75°C, 100°C, 125°C, 150°C, 175°C, 200°C, 225°C, 250°C, 275°C, and 300°C, including a helium purge for 15 min at 300°C (bottom).
- Figure 2:** TP-reaction of adsorbed mixture of (red) 5.4 mol % H-formaldehyde / 47.3 mol % H₂O / 47.3 mol % D₂O or (blue) 5.4 mol % D-formaldehyde / 47.3 mol % H₂O / 47.3 mol % D₂O over (bottom) 2%Pt/m-ZrO₂ and (top) 2.54%Na-2%Pt/m-ZrO₂. (red) H₂ and (blue) D₂.
- Figure 3:** Potential reaction mechanisms of the catalytic cycle showing the pathways for the FSR process.
- Tables:** Tabulated summary of (top) additional TP-reaction results using H₂O + H-formaldehyde or D₂O + D-formaldehyde mixtures, (middle) fixed bed catalytic reactor results, and (bottom) analysis of Figure 2.

Future Plans

Methanol Steam Reforming (MSR) and Ethanol Steam Reforming (ESR) are currently being studied as a means of hydrogen production. Prior research into the study of MSR suggests that the doping of the catalyst surface with alkalis may improve the selectivity for hydrogen production. However, FSR is a promising option for future applications of hydrogen production as it could act as a chemical carrier of hydrogen, and it could provide a way of decomposing toxic formaldehyde waste. Also, it is known that formaldehyde may be an intermediate in the MSR process and studying the effects of its performance in the FSR process could lead to new discoveries of the optimization of hydrogen production for MSR, too.

What I learned

Upon analysis of the DRIFTS and TPD-MS data, I've concluded that the alkali doping of the Pt/m-ZrO₂ Catalyst will increase basicity and promote dehydrogenation / decarboxylation in comparison to dehydration / decarbonylation by weakening the C-H bond of the formate intermediate. This is strongly suggested by the shift in the ν(CH) vibrational modes to lower wavenumber in the DRIFTS data and the decrease in the isotope effect through a rate analysis in the TP-reaction data using MS.

Skill and Experience

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

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

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