Low temperature water-gas shift: Optimization of K loading on Pt/m-ZrO$_2$ for enhancing CO conversion

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Research Area

Heterogenous catalysis is a broad field dedicated to the optimization of chemical reactions and processes by lowering the activation energy barrier towards a desired reaction. This can accelerate reaction rates, allow for milder operating conditions, and improve selectivity. The heterogeneous catalysis group at UTSA focuses on applying these concepts to important reactions related to energy and fuels, such as water-gas shift, Fischer-Tropsch synthesis, and ethanol steam reforming.

Background

Water-gas shift ($CO + H_2O \leftrightarrow CO_2 + H_2$) is an important industrial reaction used to provide a pure hydrogen source for an assortment of applications that require hydrogen, such as the Haber-Bosch process, Fischer-Tropsch synthesis, and polymer electrolyte membrane fuel cells (PEMFC). PEMFCs have become an increasingly attractive research subject for their potential to cleanly and efficiently generate electricity. Many of the processes that produce H_2 for fuel cells lead to CO production, which poisons the fuel cell. Thus, there is a need to achieve very high conversion of CO in the fuel processor. To do this, water-gas shift may be employed in two stages. First, the water-gas shift is carried out high temperatures to take advantage of kinetics. However, since the water-gas shift is exothermic, this process is equilibrium-limited, and a second stage must be conducted at low temperatures to achieve high CO conversion. Because kinetics are slow at these low temperatures, a highly active catalyst must be used, and typically a precious metal, such as Pt or Pd, supported on a partially reducible oxide, such as ZrO_2 or CeO_2, is used.

Objectives

- Determine the optimal loading of potassium for water-gas shift
- Investigate the underlying mechanism behind low temperature water-gas shift (LTS)
- Investigate the electronic effect of potassium on the C-H bond of intermediate formate
- Determine the impact of potassium loading on Pt nanoparticles on the catalyst surface

Methodology

- Catalysts were prepared using the incipient wetness impregnation (IWI) technique. An aqueous solution of tetraamineplatinum(II) nitrate was impregnated into a ZrO_2 support (63-125 um). After drying and calcining, the mother batch was split and several different potassium loadings (0.85, 1.70, 2.55, 3.40, 4.25, and 8.5 wt%) were added to the support. Subsequently, the catalysts were dried and calcined.
- Catalysts were investigated using *in-situ* DRIFTS, TPR-MS, TPD, EXAFS, and catalyst testing.
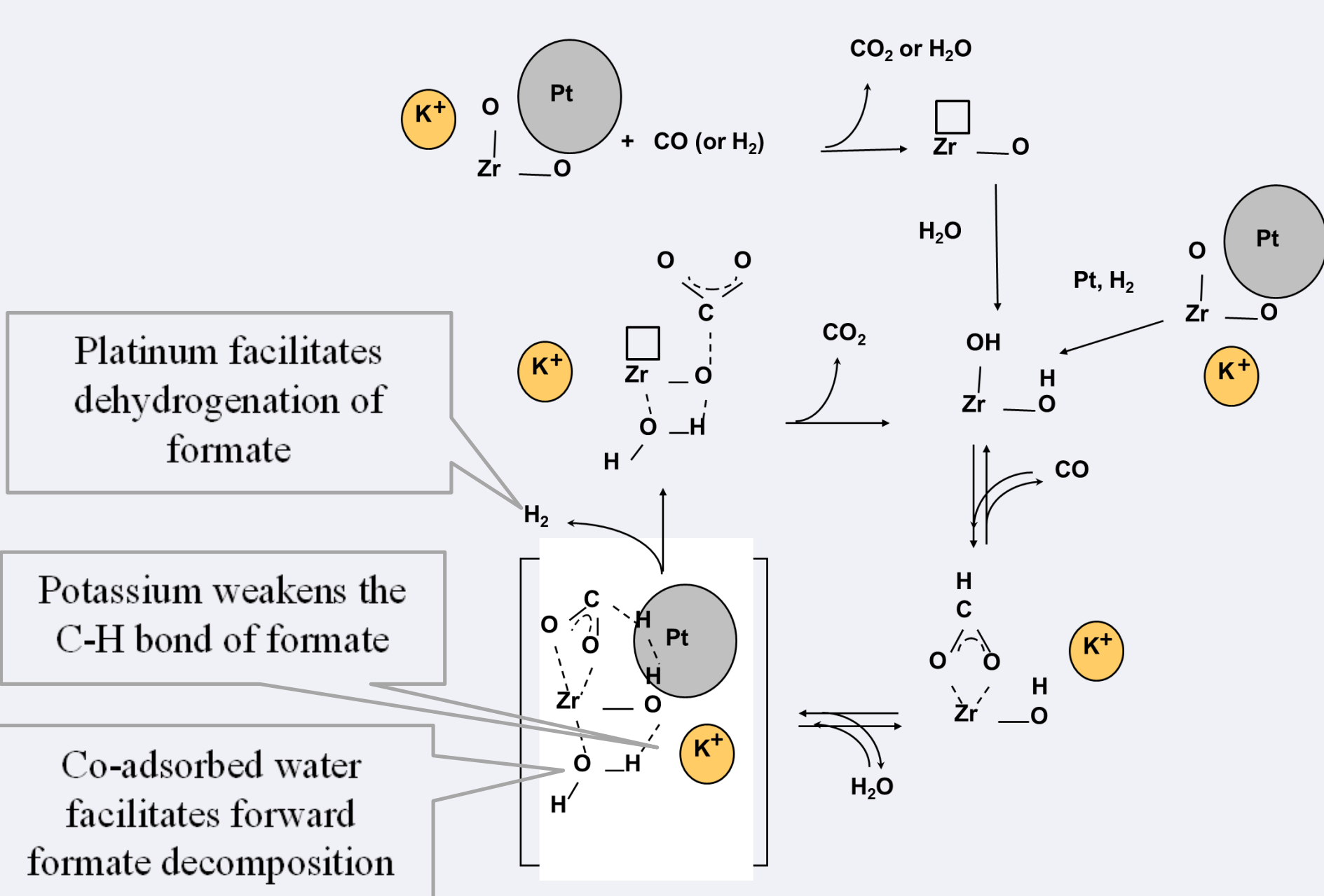
Results

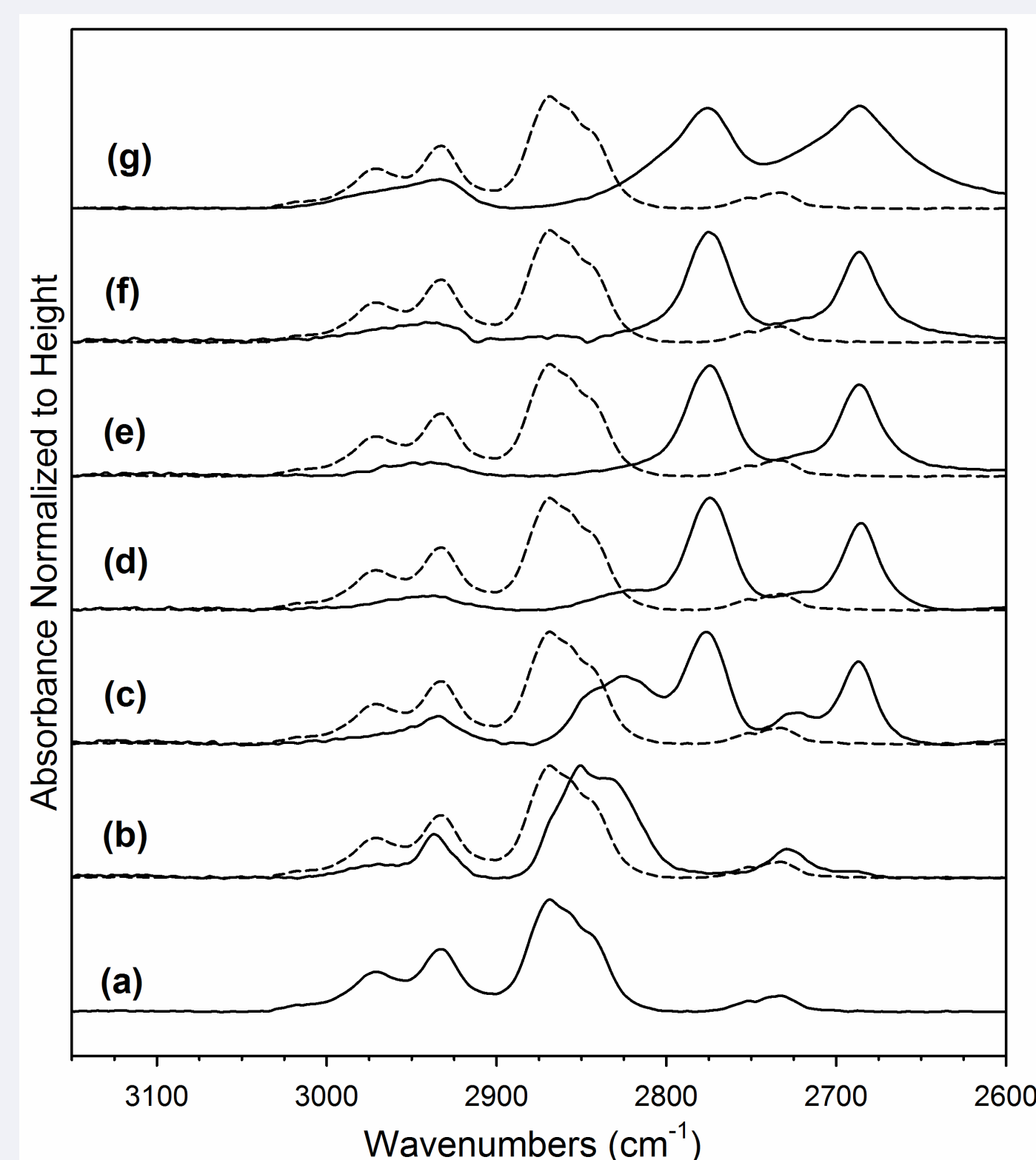**Figure 1**: Reactant-promoted associative mechanism involving formates and carbonates

Figure 2: Absorbance of the formate ν(CH) band region normalized to height of band on 2%Pt/ZrO$_2$, including: (a) 2%Pt/ZrO$_2$, (b) 0.85%K-2%Pt/ZrO$_2$, (c) 1.7%K-2%Pt/ZrO$_2$, (d) 2.6%K-2%Pt/ZrO$_2$, (e) 3.4%K-2%Pt/ZrO$_2$, (f) 4.25%K-2%Pt/ZrO$_2$, and (g) 8.5%K-2%Pt/ZrO$_2$. (Dashed lines) the reference, 2%Pt/ZrO$_2$.
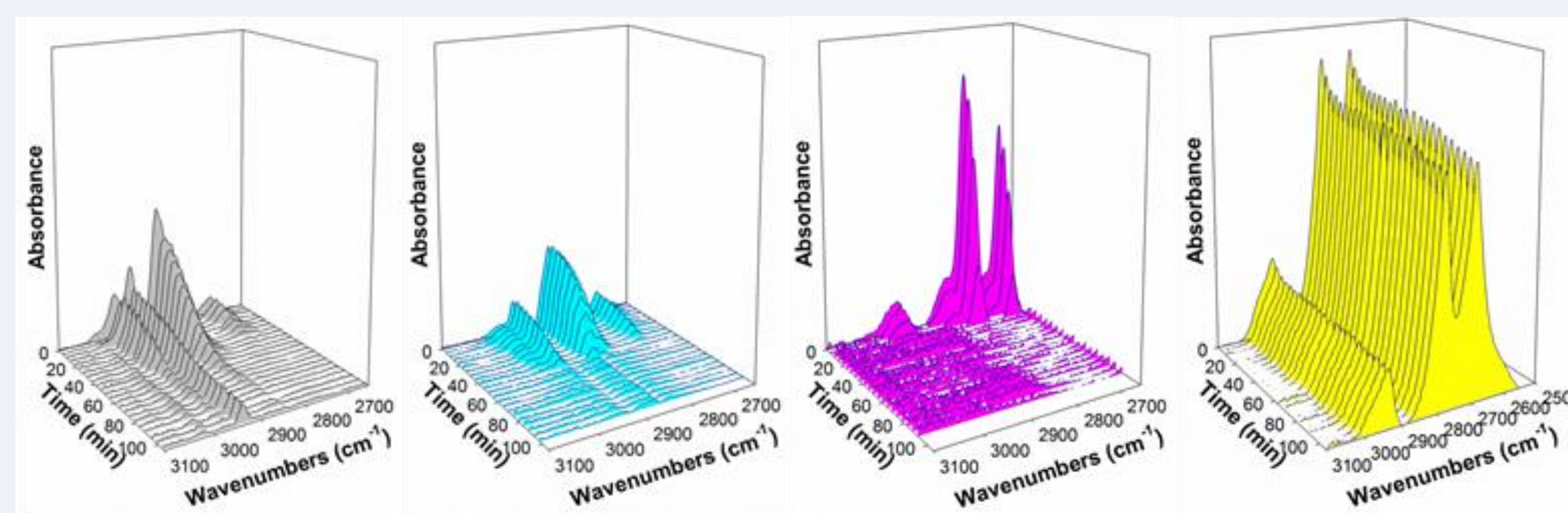

Figure 3: To scale version of formate decomposition in steam at 130 ºC, including (gray) 2%Pt/ZrO$_2$, (cyan) 0.85%K-2%PtZrO$_2$, (magenta) 2.6%K-2%Pt/ZrO$_2$, and (yellow) 8.5%K-2%Pt/ZrO$_2$.

T (°C)	2%Pt/ZrO$_2$	0.85% K -2%Pt/ZrO$_2$	2.55% K - 2%Pt/ZrO$_2$	3.4% K -2%Pt/ZrO$_2$	4.25% K - 2%Pt/ZrO$_2$	8.5% K - 2%Pt/ZrO$_2$
300	73.3	70.03	100	69.4	68.5	20.1
285	54.5	52.4	78.9	51.7	49.6	12.9
260	32.9	30.2	43.2	31.7	28.6	7.2

Table 1: carbon monoxide conversion during LT-WGS for different potassium doping quantities (26.1% H$_2$O, 2.9% CO, 29.9% H$_2$, 4.3% N$_2$ (balance He) at P = 1 atm, SV = 167,638 Ncc/h/g$_{cat}$)

Figure 1 shows the proposed mechanism for the water-gas shift mechanism. The breaking of the formate C-H bond is the rate-limiting step of LTS, and potassium promotion helps weaken this bond. Figure 2 shows the absorbance of the formate ν(CH) band; at higher loadings, the band shifts to lower wavenumbers, indicating that the bond is weakening, likely due to electronic donation by potassium. Figure 3 shows formate decomposition in steam over time as measured by DRIFTS. For the optimum loading or 2.6 wt.%, the formate decomposes most rapidly. At excessive loadings, potassium covers the surface of the Pt nanoparticles, inhibiting their role in hydrogen transfer reactions. This leads to slower decomposition of formate. Table 1 shows the CO conversion obtained in reactor studies. At the optimum loading, the highest CO conversion in attained.

Skills and Experience

- DRIFT spectroscopy
- Data analysis and processing with Excel
- Data reduction with Python

What I Learned

I discovered that 2.6 wt.% is the optimal potassium loading for the tested catalysts for LTS. At this loading, there is enhanced CO conversion as well as quick reaction. Additionally, I learned likely mechanisms of the water-gas shift reaction and became more well-versed in the spectroscopic techniques used in heterogeneous catalysis.

Future Plans

In the future, we plan to test other alkali promoters for the water-gas shift reaction. Our group has yet to perform a loading study with lithium as a dopant. Additionally, it is possible our group will branch to studying cesium or alkaline earth metals as potential promoters for this catalyst system. Additionally, this family of catalysts could be tested for efficacy during related reactions such as ethanol steam reforming, and methanol steam reforming.

Acknowledgments

References

Watson, C.D., Martinelli, M., Cronauer, D.C., Kropf, A.J., Marshall, C.L., Jacobs, G., "Low temperature water-gas shift: Optimization of K loading on Pt/m-ZrO$_2$ for enhancing CO conversion," Applied Catalysis A: General 598 (2020) 17 pp. https://doi.org/10.1016/j.apcata.2020.117572

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