Effect of Pt precursor on the stability of Pt/CeO2/MgAl2O4 catalysts in ethanol steam reforming

Braedon McFee, Gary Jacobs
Department of Chemical Engineering
College of Engineering, The University of Texas at San Antonio

UTSA
1 UTSA Circle, San Antonio, TX 78249

ABSTRACT

Studies show that the increase in pollutants entering the earth's atmosphere has caused a rise in the temperature of the earth's air and oceans, making July of 2023 the hottest month ever recorded. It has become clear that decreasing the number of pollutants entering the earth's atmosphere is a top priority, and one way of accomplishing this is through using renewable fuels. One reaction that uses renewable sources, such as corn (USA) and sugar cane (Brazil) to produce H_2 fuel, is the steam reforming of ethanol. This research focuses on improving the stability of $Pt/CeO_2/MgAl_2O_4$ catalysts for the ethanol steam reforming (ESR) reaction. The three main variables of importance for developing these catalysts were the acidity of the support, the redox properties, and the Pt precursor salt. As the support acidity increases, undesired reaction pathways will occur on the acid sites, causing decreased selectivity to H_2 and a higher catalyst deactivation rate. Pertaining to the redox properties, LC-XANES showed that activation at the reaction temperature resulted in partial reduction of Ce^{4+} to Ce^{3+}. To determine which Pt precursor offered the best stability, reaction testing and in-situ infrared (IR) spectroscopy during steady state ESR were used. IR spectroscopy experiments showed that the catalyst prepared using tetraammine platinum hydroxide had the best stability and the lowest buildup in the inventory of intermediates. Our findings indicate that the low acidity $CeO_2/MgAl_2O_4$ support and the tetraammine platinum hydroxide precursor provided the best stability for ESR.

INTRODUCTION

Non-Renewable resources, such as coal and oil, are a major contributor to the increasing problem of climate change. When these fossil fuels are burned they release a large amount of greenhouse gases with the primary gas being carbon dioxide. Since these non-renewable resources are providing about 80% percent of the worlds energy, a large amount of these fossil fuels are being burned and is why the emissions from these resources are the primary cause of global warming. For these reasons it is vital that the world determines a way of producing energy from renewable sources such as hydrogen from biomass. Hydrogen can be created from the combination of an ethanol steam reforming reaction and water gas shift reaction, meaning it is important to explore catalysts that will optimize the formation of ethanol from biomass. This research analyzes the factors of support acidity, redox properties, and Pt precursor salt and compares them to determine which catalyst provides the most stability for the ethanol steam reforming reaction.

METHODS

The procedure for determining which Pt precursor offered the best stability consisted of reaction testing in a fixed bed microreactor and in-situ infrared (IR) spectroscopy during steady state ESR. IR spectroscopy provided a means of determining functional groups contained within the molecule. This allowed for an analysis on the buildup of ESR intermediates (e.g., acetate) on the active support as a function of time.
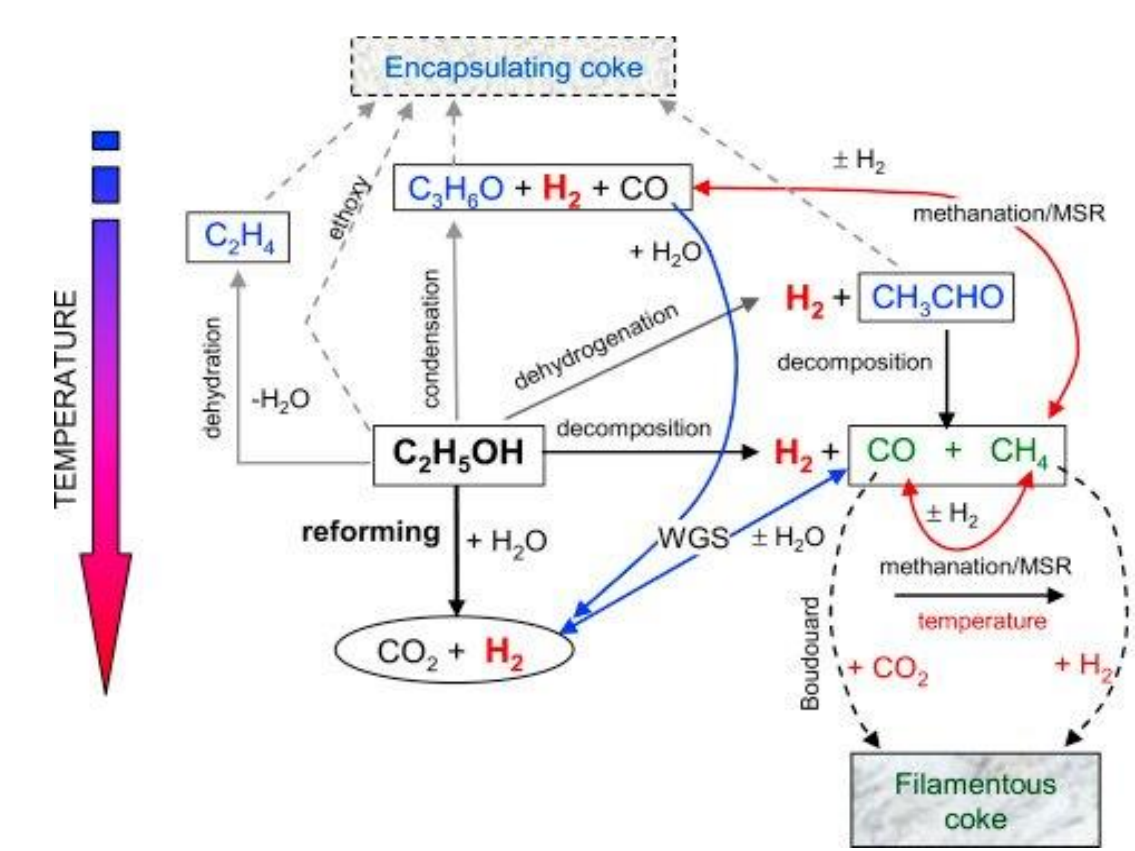
RESULTS

Figure 1. Side reactions that can occur in the steam reforming of ethanol
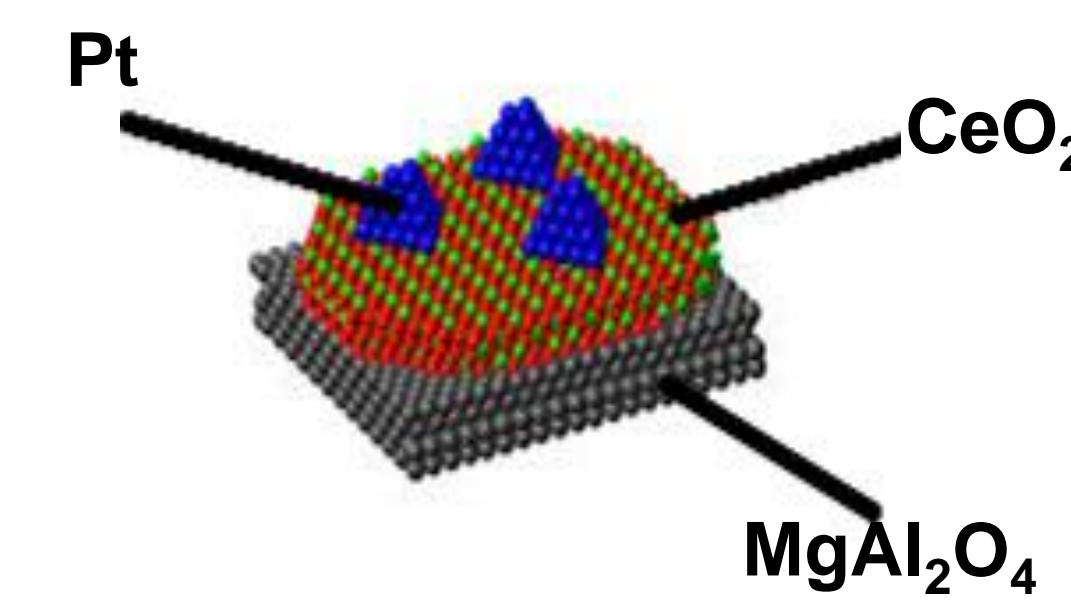

Figure 2. Visual representation of catalyst
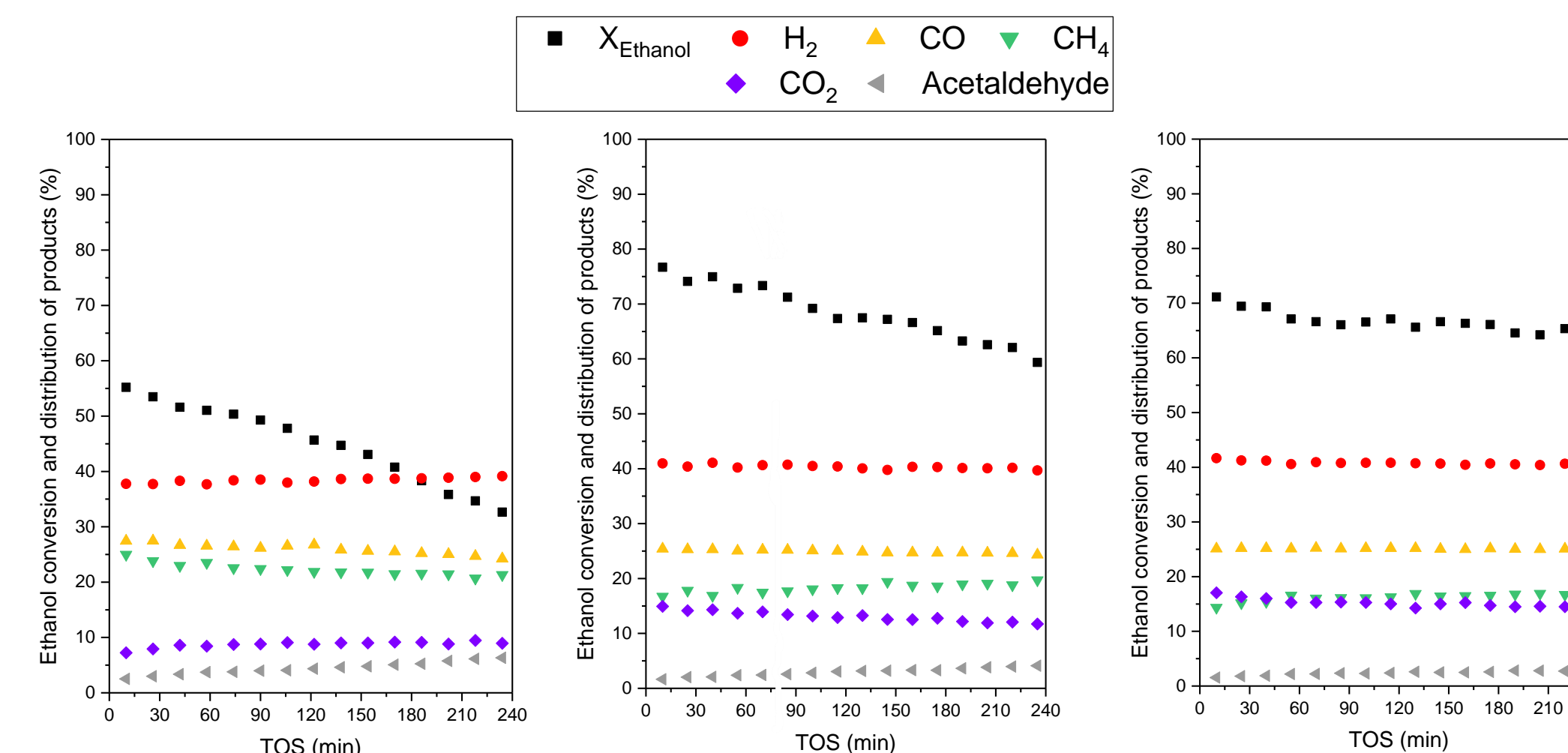

Figure 3. Conversion of ethanol and product evaluation over a period of time for each Pt precursor, Cl, NO3, OH
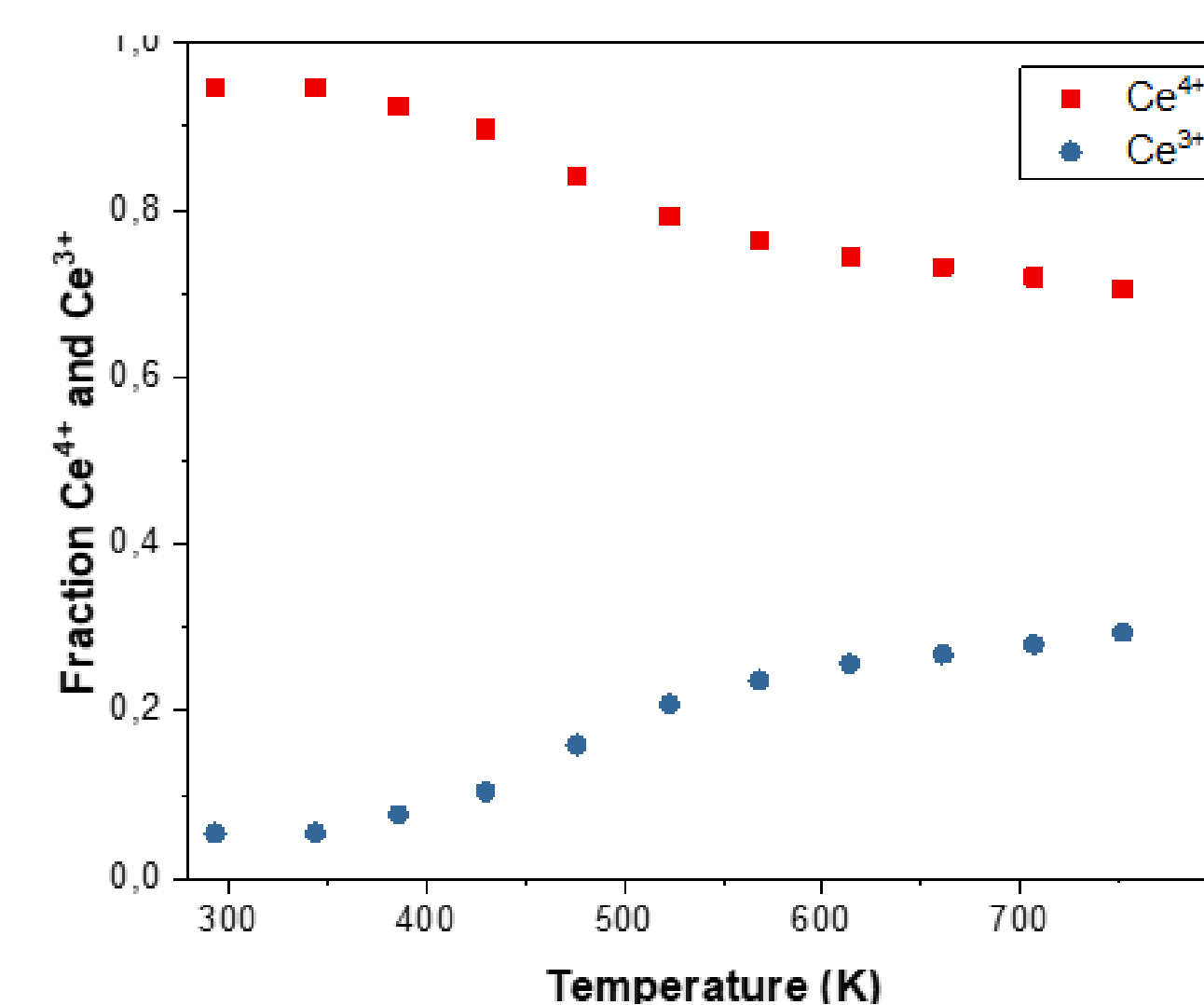

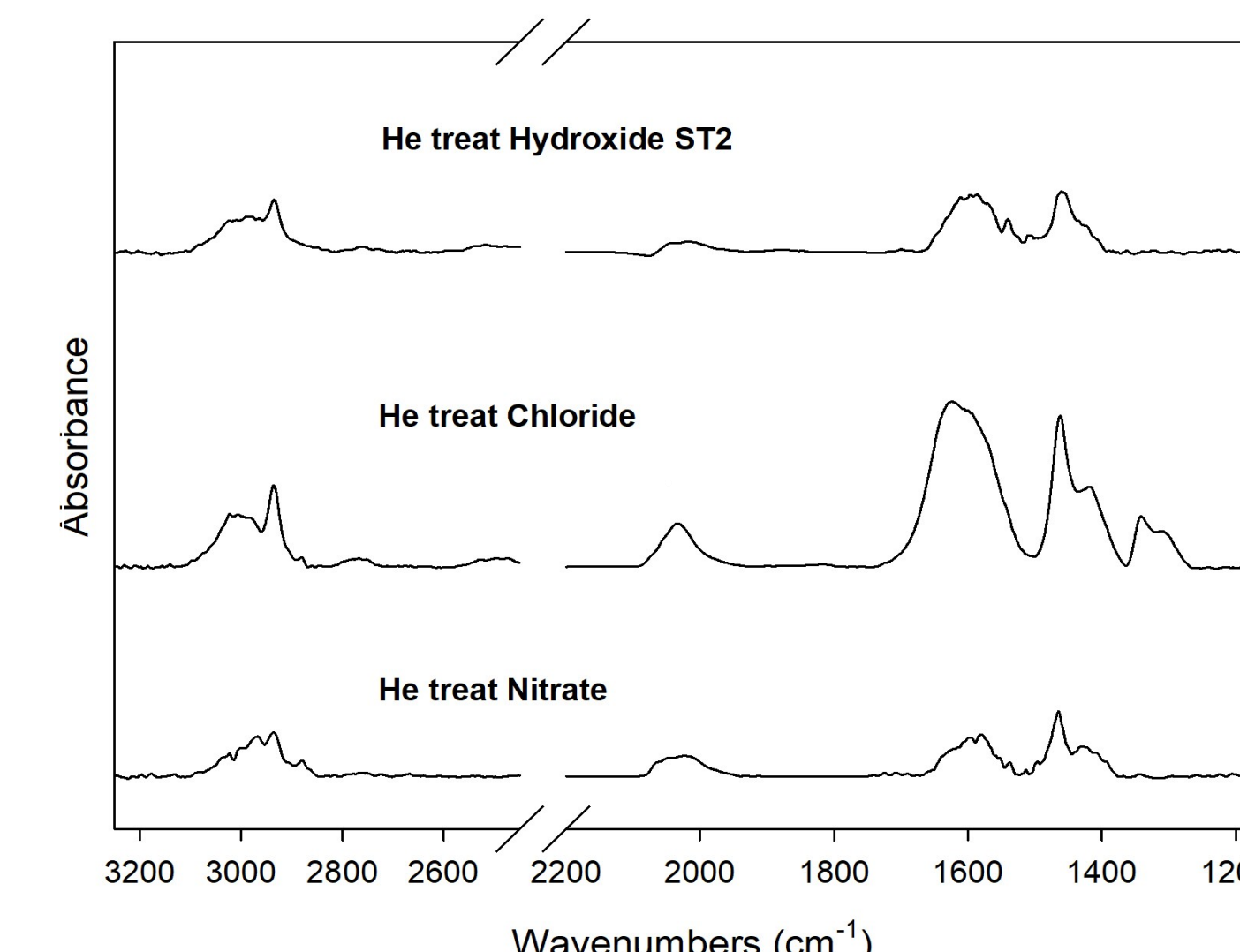**Figure 4.** LC-XANES recording for Ce fraction

Figure 5. IR spectral difference between the final scan and the third point of ethanol steam reforming run

RESULTS

From the figure comparing the spectral difference in scans of the ethanol steam reforming, it is shown that a significant buildup of intermediates, such as acetate, is occurring. Acetate can be seen in Figure 5 with C-H vibrations, 2800 cm-1 – 3100 cm-1 range, and OCO vibrations, 1100 cm-1 – 1600 cm-1 range, with the asymmetric configuration occurring at the higher wavenumber and symmetric at the lower wavenumber. The reaction occurring is at the junction between the partially reduced oxide support, ceria, and the metal nanoparticle, Pt. The acetate is sitting on the partially reduced ceria support, and it is being operated on by Pt. The Pt wants to pull off the CH3- from acetate, pull off H- from the support, and then do more dehydrogenation on the Pt surface. Meaning, if the Pt deactivates in any way, such as sintering or coking, there is less exposed Pt for the catalysis, and the "steady state" inventory of acetate intermediate will tend to increase on the surface of the catalyst with time. In Figure 5, the Chloride precursor is experiencing the greatest buildup of acetate over time due to the high peaks from the 2800 cm–1 – 3100 cm–1 and the 1100 cm–1 – 1600 cm–1 range.

CONCLUSION

The goal of determining the most optimal Pt precursor in the ethanol steam reforming reaction was accomplished. The findings were that the hydroxide precursor provided better stability than the chloride or nitrate precursors. These findings are important because stability of the Pt precursor will allow for a more consistent conversion of ethanol. Meaning the catalyst won't deactivate from sintering or coking, and the production of hydrogen will be consistent. Our findings indicate that the low acidity $CeO_2/MgAl_2O_4$ support and the tetraammine platinum hydroxide precursor provided the best stability for ESR.

REFERENCES/ACKNOWLEDGEMENTS

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