UTSA

Effects of Alkali Doping on Ag/m-ZrO$_2$ Catalyst in Methanol Steam Reforming

C. Eaton and G. Jacobs
The University of Texas at San Antonio, San Antonio TX, 78249

Abstract

Through methanol steam reforming (MSR), methanol may be efficiently be converted to H$_2$, a clean and desirable fuel for fuel cell applications. However, unpromoted metal/m-ZrO$_2$ catalysts have been found to exhibit selectivity for an undesired pathway involving decarbonylation of the surface formaldehyde intermediate, resulting in less H$_2$ production per cycle. Catalysts need to be developed that can improve the H$_2$ selectivity of reaction for this process. In a previous study, alkali doping improved the performance of Pt/m-ZrO$_2$ catalyst through a H$_2$-selective mechanism involving dehydrogenation and decarboxylation of the formate intermediate. In this research, the focus was on replacing Pt with less expensive Ag. To test if this was feasible, Alkali doping of 1.1 At.% Ag/m-ZrO$_2$ was conducted to reach 0.5, 1.0, 1.8, 2.5, and 5 wt. % Na. Alkali doping of Ag/m-ZrO$_2$ was effective at increasing the selectivity of the desired pathway and decreasing the temperature of H$_2$ evolution. Future reactor tests will be performed to discover how alkali doped Ag/m-ZrO$_2$ compares to doped Pt/m-ZrO$_2$.

Introduction

Hydrogen is a very attractive alternative fuel due to its high energy density and low environmental impact, particularly through the application of fuel cells. One pathway of hydrogen production is methanol steam reforming where methanol is converted to hydrogen and carbon dioxide with high efficiency. Previous studies on alkali doping a Pt/m-ZrO$_2$ catalyst showed that increasing the surface basicity weakens the C-H bond of the formate intermediate which increases production of H$_2$ and promotes the desired chemical pathway. Since there has been limited research on catalysts for MSR, there is the possibility of discovering a less expensive catalyst that can perform with desired activity and selectivity.

Purpose

The purpose of this research is to discover if an alkali doping of Ag/m-ZrO$_2$ catalyst can improve the H$_2$-selectivity in methanol steam reforming with the eventual goal of replacing Pt in the current catalyst with the lower cost Ag metal.

Methods

The catalyst was synthesized by crushing and sieving m-ZrO$_2$ pellets to 63-106 μm. Silver Nitrate was then added to the point of incipient wetness and the catalyst was dried and calcined which resulted in 1.1% atomic percent Ag/m-ZrO$_2$. The same process was repeated with Sodium nitrate to dope the catalyst with 0.5, 1.0, 1.8, 2.5, and 5 weight percent sodium.

The finished catalyst was tested and characterized by H$_2$-Temperature Programmed Reduction (TPR), CO$_2$ Temperature Programmed Desorption with Mass Spectrometry, DRIFTS of steam reforming of methanol, and temperature programmed surface reaction of methanol steam reforming.

Results

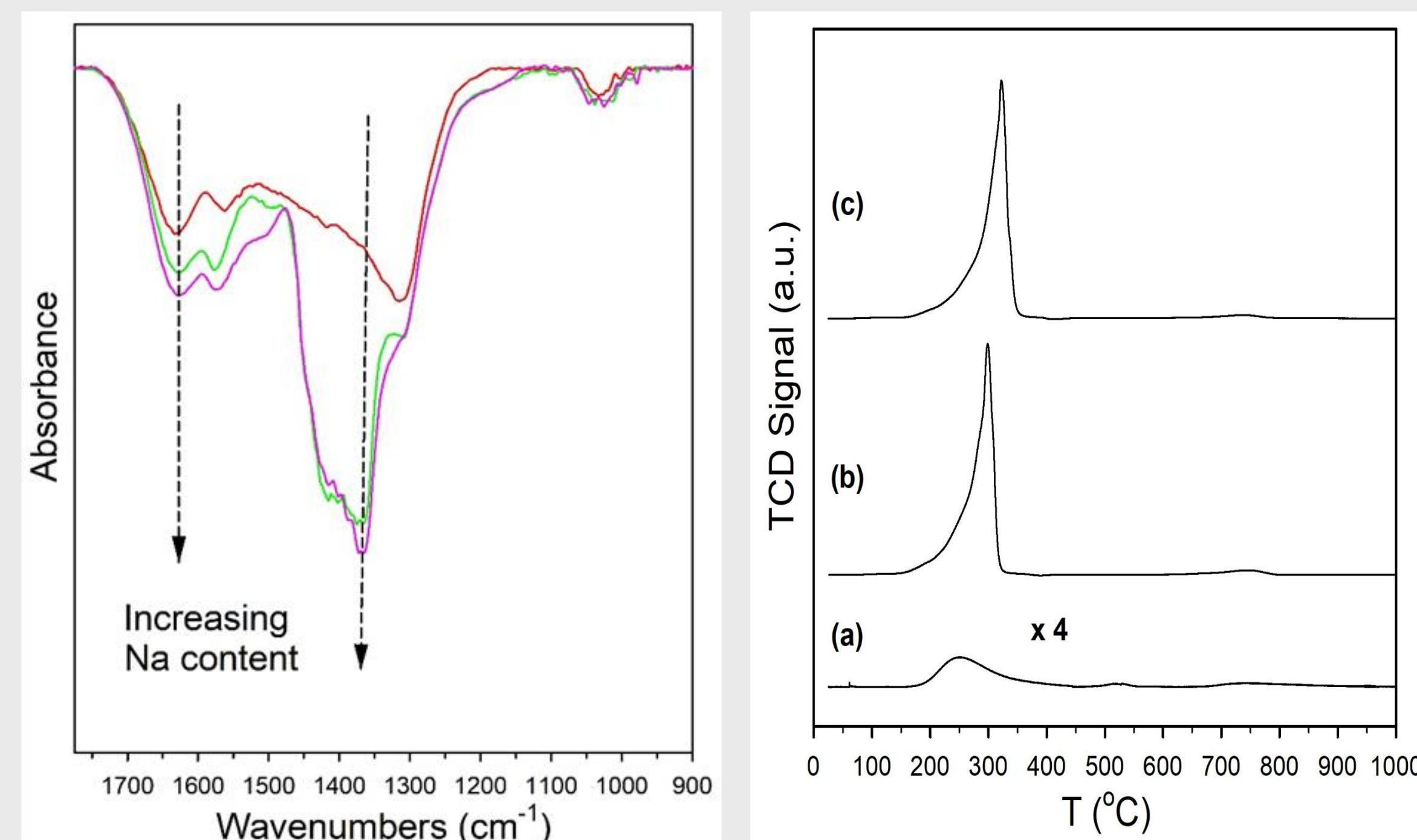### Catalyst activation - IR Spectroscopy and H$_2$-TPR

Figure 1: (left) Carbonate removal of (red) unpromoted 1.1%Ag/m-ZrO$_2$ and the same with (green) 1.8%Na and (pink) 2.5%Na. (right) H$_2$-TPR. Catalyst activation involves reduction of Ag$_2$O to Ag^0 followed by Ag-catalyzed carbonate removal and partial reduction of m-ZrO$_2$, which forms bridging OH groups at Zr^{3+} defects.

Infrared spectroscopy at various stages of MSR reveal that the addition of sodium favors the desired pathway depicted in Figure 4.

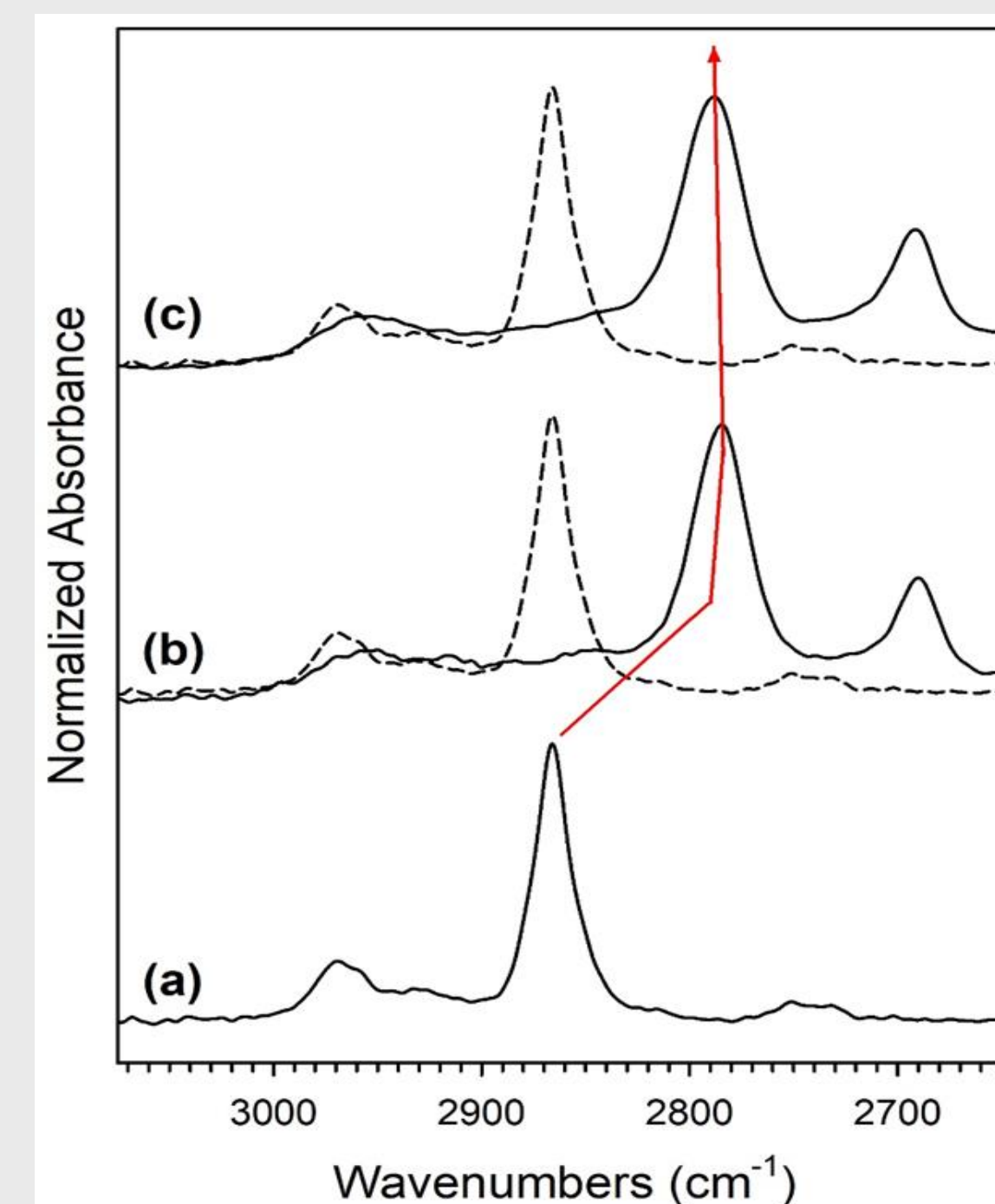### Infrared Characterization of Main ν(CH) Band

H$_2$ Production in MSR at Select Temperatures

Figure 2: Main ν(CH) band of (spectrum a and dash-lined reference spectra) unpromoted 1.1%Ag/m-ZrO$_2$ and the same catalyst doped with (b) 1.8%Na and (c) 2.5%Na.

Other results from the infrared spectroscopic analysis show that the addition of Na lowers the wavenumber of the main ν(CH) band of formate. This indicates weakening of the formate C-H bond making it easier to release H$_2$. This change is the result of increased basicity of the catalyst that causes the -OOC portion of the formate to adhere strongly to the surface of the catalyst, weakening the C-H bond.
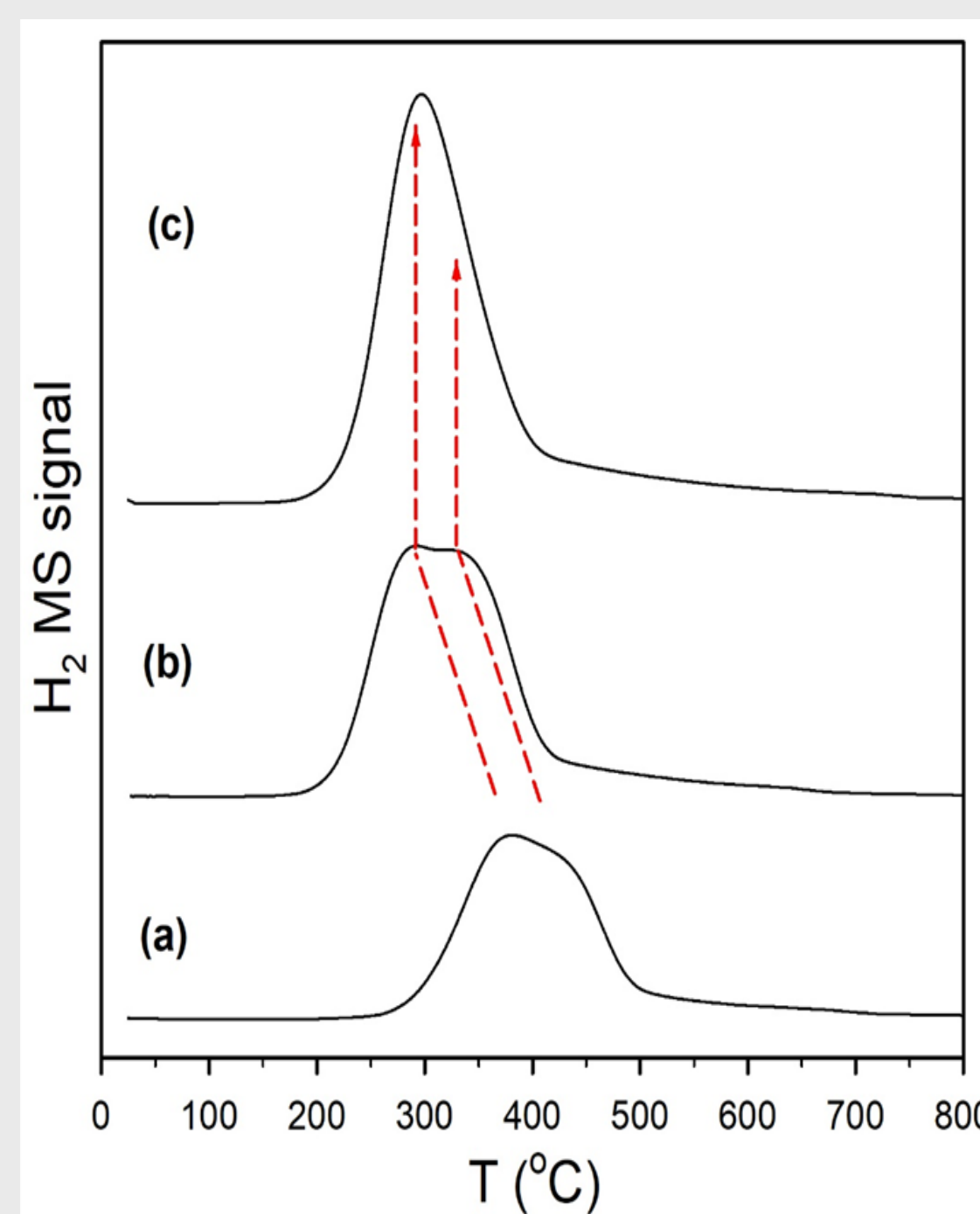
Figure 3: H$_2$ evolution in temperature-programmed MSR using pre-adsorbed methanol and H$_2$O for (a) unpromoted 1.1%Ag/m-ZrO$_2$ and the same catalyst doped with (b) 1.8%Na and (c) 2.5%Na.

The addition of sodium and increasing sodium concentration results in greater production of hydrogen at lower temperatures. This is achieved through the promotion of the desired chemical pathway that moves away from formaldehyde decomposition by decarbonylation to formate formation and decomposition by decarboxylation / dehydrogenation.

Results - con't

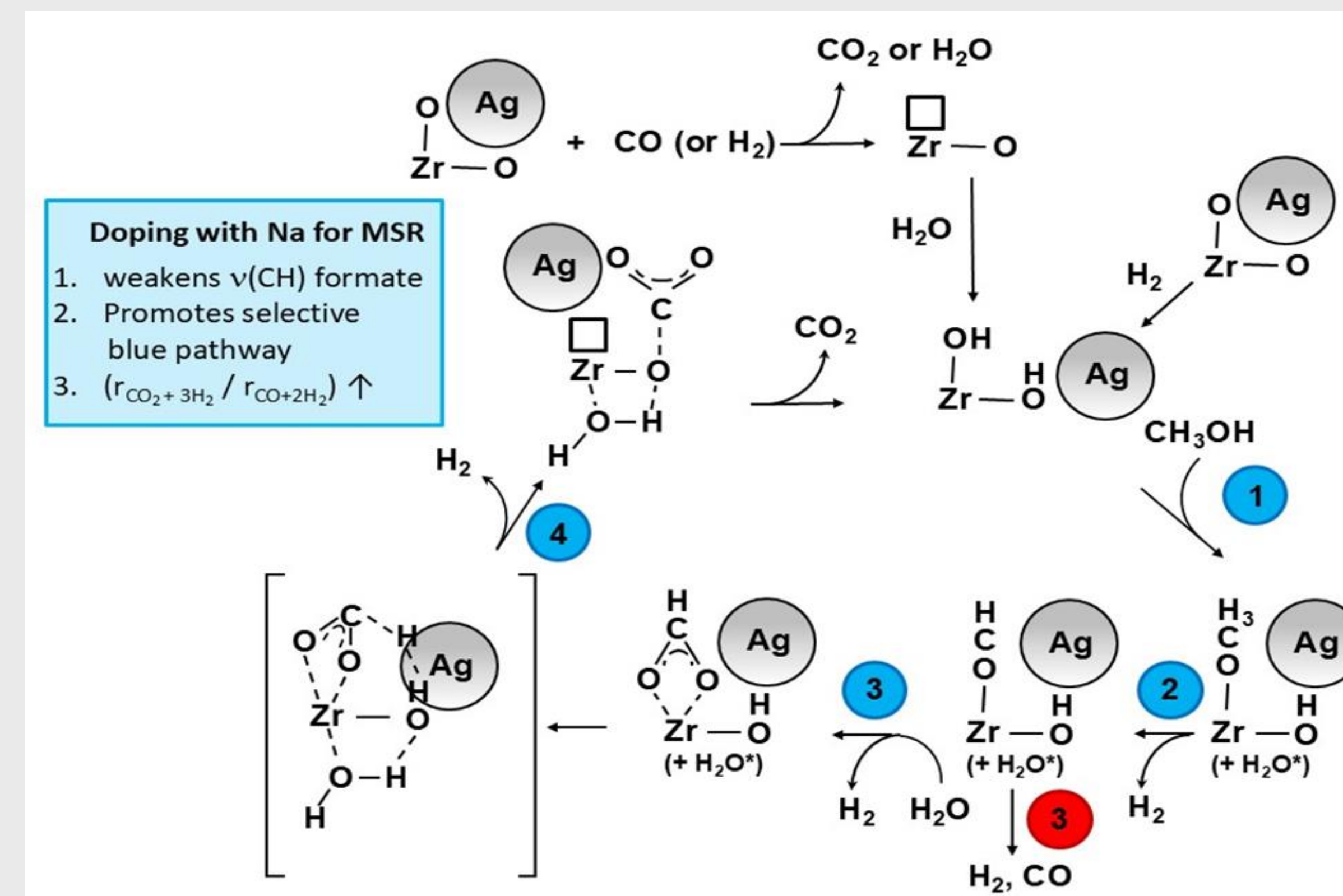### Proposed Mechanism for Na-Ag/m-ZrO$_2$ in MSR

Figure 4. Proposed mechanistic effect of Na during MSR over Na-Ag/m-ZrO$_2$ catalyst.

This graphic summarizes previous data and offers an explanation about how the addition of sodium effects the chemical pathway. Most notably, it shows where the desired path deviates from the undesired; specifically, where the pathway moves away from formaldehyde decomposition by decarbonylation to formate formation and decomposition by decarboxylation / dehydrogenation. Tuning the catalyst at these crucial steps could assist in the discovery of cheaper and more efficient catalysts that could make MSR much more feasible.

Conclusions

➤ Alkali doping of an Ag/m-ZrO$_2$ catalyst promotes the desired H$_2$-selective pathway and decreases the temperature of H$_2$-evolution during MSR.

➤ The increased performance of the Na-Ag/m-ZrO$_2$ catalyst is strongly linked to the increased basicity of the catalyst surface, which increases the strength of the interaction between the –O$_2$C functional group of formate and, in turn, weakens the C-H bond, promoting dehydrogenation.

➤ Future research in a fixed bed microreactor will be conducted to determine how this catalyst performs comparatively to other MSR catalysts such as Na-Pt/m-ZrO$_2$.

References

Michela Martinelli, Jonas Marcelle, Donald C. Cronauer, A. Jeremy Kropf, Gary Jacobs. **Isotope effect in formaldehyde steam reforming on Pt/m-ZrO$_2$: Insight into chemical promotion by alkalis.** https://doi.org/10.1016/j.catcom.2023.106668

Lin, L., Zhou, W., Gao, R. et al. **Low-temperature hydrogen production from water and methanol using Pt/α-MoC catalysts.** Nature 544, 80–83 (2017). https://doi-org.libweb.lib.utsa.edu/10.1038/nature21672

Acknowledgements