

Background

- Hydrogen is a very renewable source of energy to be used in fuel cells. However, the process to obtain that hydrogen is complex. In addition to that it is also hard to store.
- One of the ways to obtain that hydrogen is through a reaction that involves the reforming of light alcohols into hydrogen. The selective reaction involves reacting the light alcohols with water to form carbon dioxide and hydrogen, while the unselective reaction produces carbon monoxide and less hydrogen:



- The reaction requires a catalyst, and that catalyst needs to have the properties necessary to facilitate the desired reaction. Previous studies have shown that using a Pt/m-ZrO₂ catalyst doped with Na alkali increases the selectivity of the reaction to promote hydrogen production. This research shows how the selectivity is affected by using lithium doping, including the effect of Li content.

Methodology

Catalyst Preparation

- First, the catalyst had to be prepared. 2%Pt/m-ZrO₂ was prepared by loading monoclinic ZrO₂ (1/8" pellets, Alfa Aesar, crushed and sieved to 63–106 μm) with an aqueous solution of tetraamine platinum (II) nitrate (Alfa Aesar) to the point of incipient wetness. The catalyst was dried and calcined in air using a muffle furnace. This mother batch was divided into several batches for adding different weight % Li loadings with Li(NO₃) (Alfa Aesar) as the precursor. Aqueous incipient wetness impregnation was also used to add the lithium, with drying and calcination

H₂-Temperature Programmed Reduction (TPR) and TPR-mass spectrometry

- An Altamira AMI-300R unit equipped with a thermal conductivity detector (TCD) was used to record temperature programmed reduction (TPR) profiles of the catalysts. 10 % H₂ in Ar (UHP, Airgas) was flowed, and the temperature was increased from 30 to 1000 °C. The thermocouple was located inside the catalyst bed. Approximately 200 mg of sample were used.

Temperature Programmed Desorption with Mass Spectrometry

- CO₂ temperature programmed desorption (CO₂-TPD) was investigated using an Altamira AMI-300R instrument connected to a Hiden Mass Spectrometer. Firstly, the catalyst was reduced at 300 °C using H₂ and argon for 1 h. The sample was cooled to 225 °C in H₂, saturated with H₂O by bubbling He through a saturator (held at ambient temperature) for 15 min to ensure bridging OH group formation, and further reduced at 225 °C in H₂/Ar mixture for 15 min. Then, at 50 °C, the sample was saturated with CO₂ for 15 min, and finally the temperature was increased to 500 °C in helium while the MS signal of CO₂ was followed.

DRIFTS of steam reforming of methanol

- A Nicolet iS-10 Fourier Transform infrared spectrometer was used to conduct temperature stepped methanol steam reforming reaction experiments. First, 512 scans were taken of the calcined catalyst in flowing helium at ambient temperature. The catalyst was reduced at 300°C using a 1:1 mixture of H₂:He for 1 h and a background spectrum of 512 scans was taken. The catalyst was purged in helium at 300°C, and then cooled to 50°C in the flowing He and another background of 512 scans was taken. Helium was used to bubble methanol for ~15 min. Then, helium was used to remove the gas phase and weakly adsorbed methanol species and a spectrum of 512 scans was taken. Helium was bubbled through a saturator (located in a 31°C water bath) containing deionized H₂O, resulting in an H₂O concentration of 4.4% with a flow rate of 30 cm³/min. This resulted in a reaction between adsorbed H₂O and methoxy species, converting them to formate, followed by decarbonylation/ decarboxylation of formate. The Li content was varied, and the temperature was stepped in 25°C increments from 50°C to 350°C.

Temperature programmed surface reaction of methanol steam reforming

- Catalysts were activated by (1) flowing 33% H₂ (balance argon) at 300 °C, (2) cooling to 225 °C and steaming for 15 min using helium flowed through a H₂O saturator, (3) flowing 33% H₂ (balance argon) at 225 °C H₂ for 10 min, and (4) purging in argon for 15 min and cooling to 50°C. The procedure was performed to ensure that defect-associated bridging OH groups were formed on the surface of the catalyst, which is more representative of the catalyst surface during steam reforming catalysis at a high H₂O/CH₃OH ratio.

Figures and Results

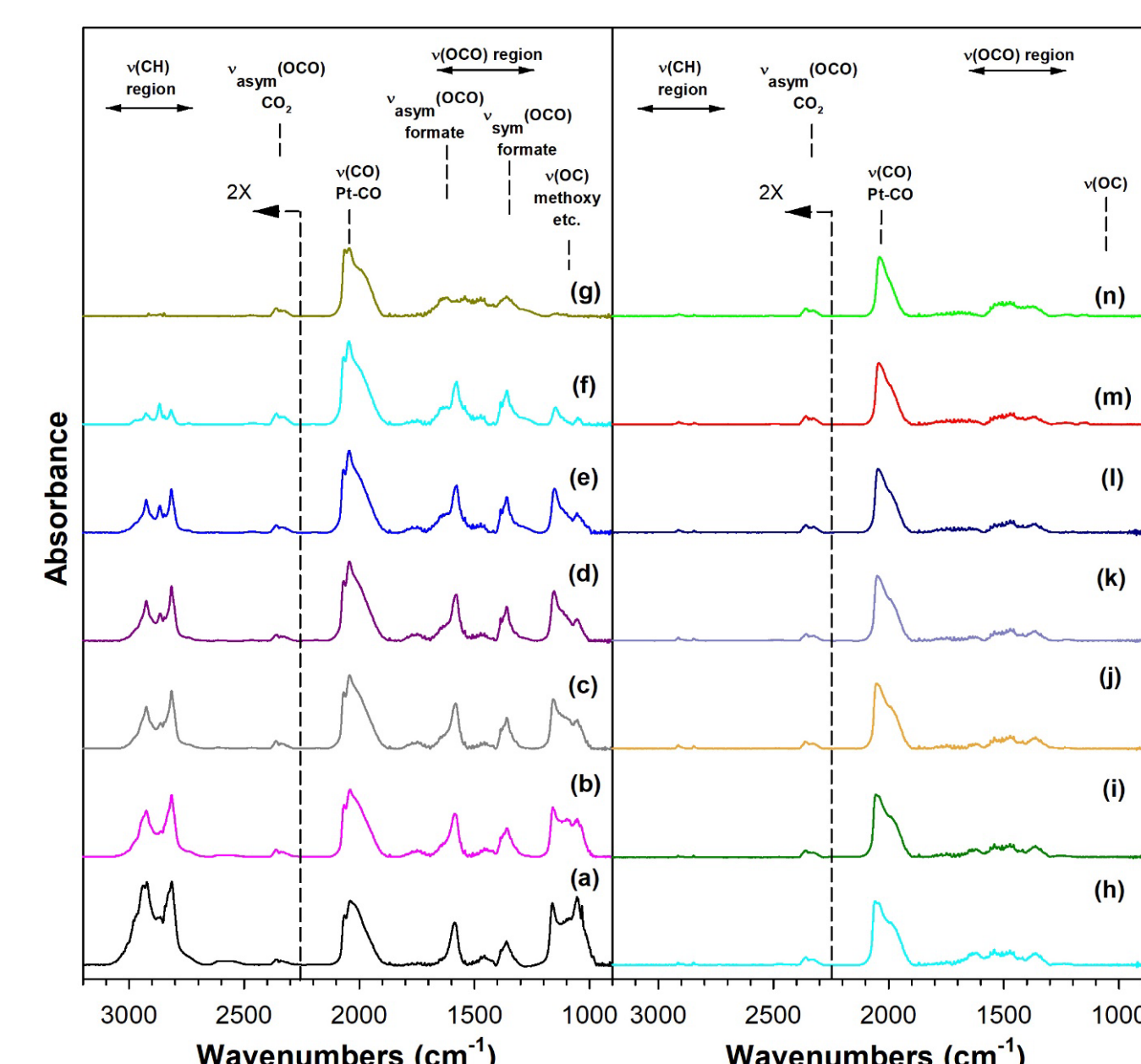


Figure 1: DRIFTS of (a) adsorbed methanol at 50°C, and temperature stepped steam reforming of adsorbed methanol in 30 cm³/min of 4.4% H₂O (balance He) over 2%Pt/m-ZrO₂ at (a) 50°C, (b) 75°C, (c) 100°C, (d) 125°C, (e) 150°C, (f) 175°C, (g) 200°C, (h) 225°C, (i) 250°C, (j) 275°C, (k) 300°C, (l) 325°C, (m) 350°C, and (n) 350°C (He purge for 10 min).

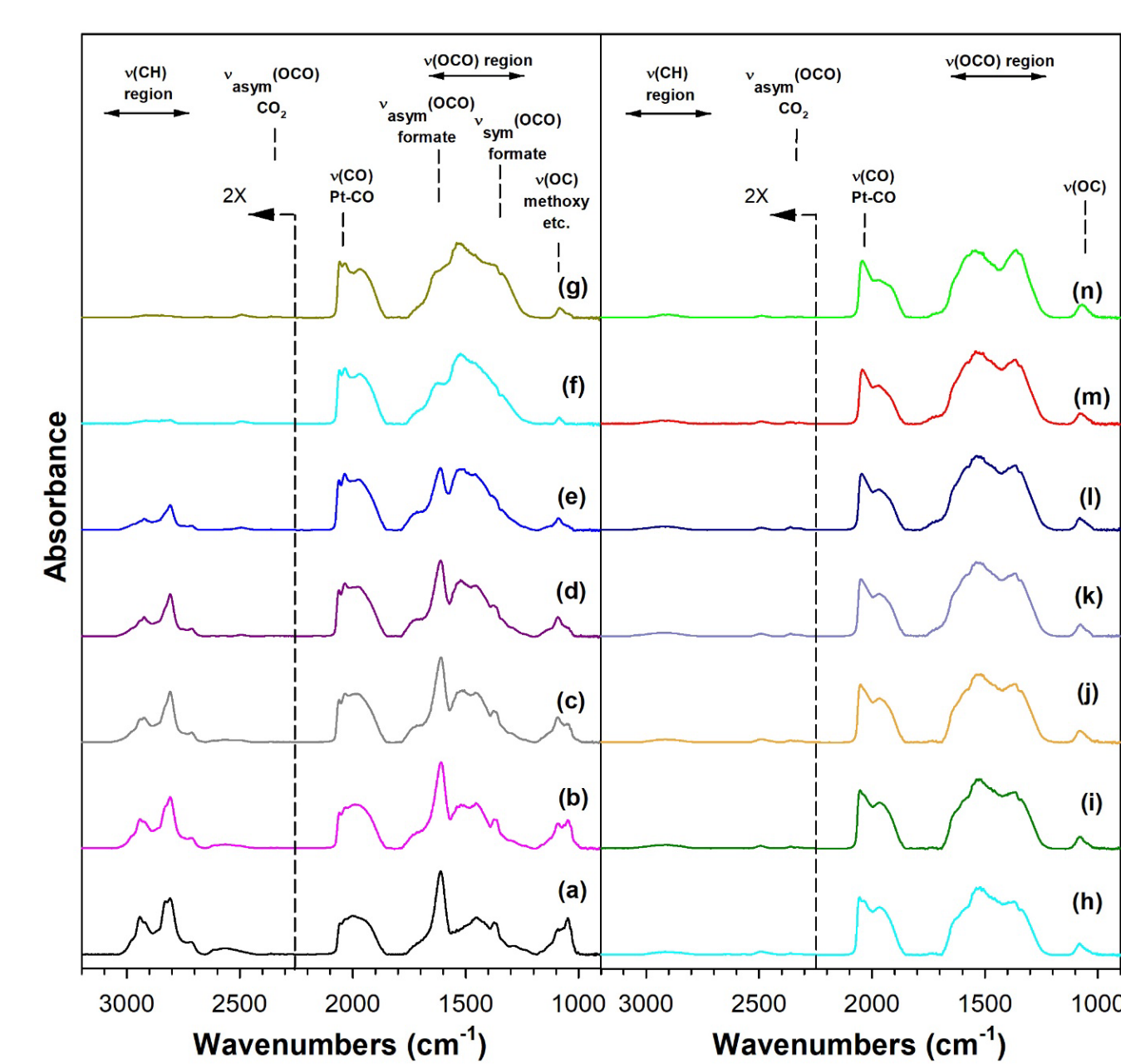


Figure 3: DRIFTS of (a) adsorbed methanol at 50°C, and temperature stepped steam reforming of adsorbed methanol in 30 cm³/min of 4.4% H₂O (balance He) over 0.75%Li-2%Pt/m-ZrO₂ at (a) 50°C, (b) 75°C, (c) 100°C, (d) 125°C, (e) 150°C, (f) 175°C, (g) 200°C, (h) 225°C, (i) 250°C, (j) 275°C, (k) 300°C, (l) 325°C, (m) 350°C, and (n) 350°C (He purge for 10 min).

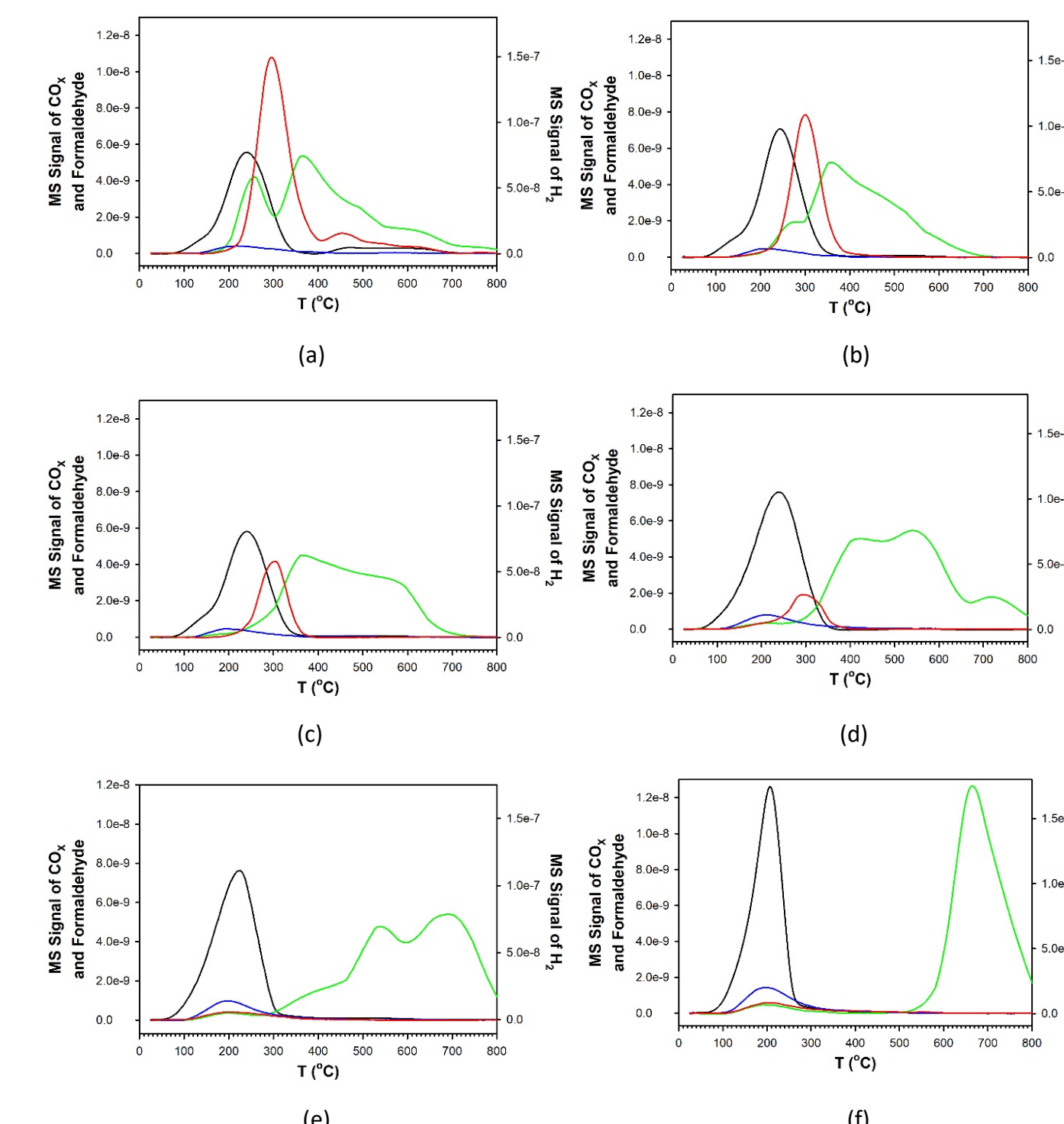


Figure 5: Temperature programmed surface reaction of methanol steam reforming, including (a) unpromoted 2%Pt/m-ZrO₂, and the same with (b) 0.15% Li, (c) 0.30% Li, (d) 0.54% Li, (e) 0.75% Li, and (f) 1.5% Li. Chemical species evolved include on the right axis (black) H₂ and, on the left axis, (red) CO, (green) CO₂, and (blue) formaldehyde.

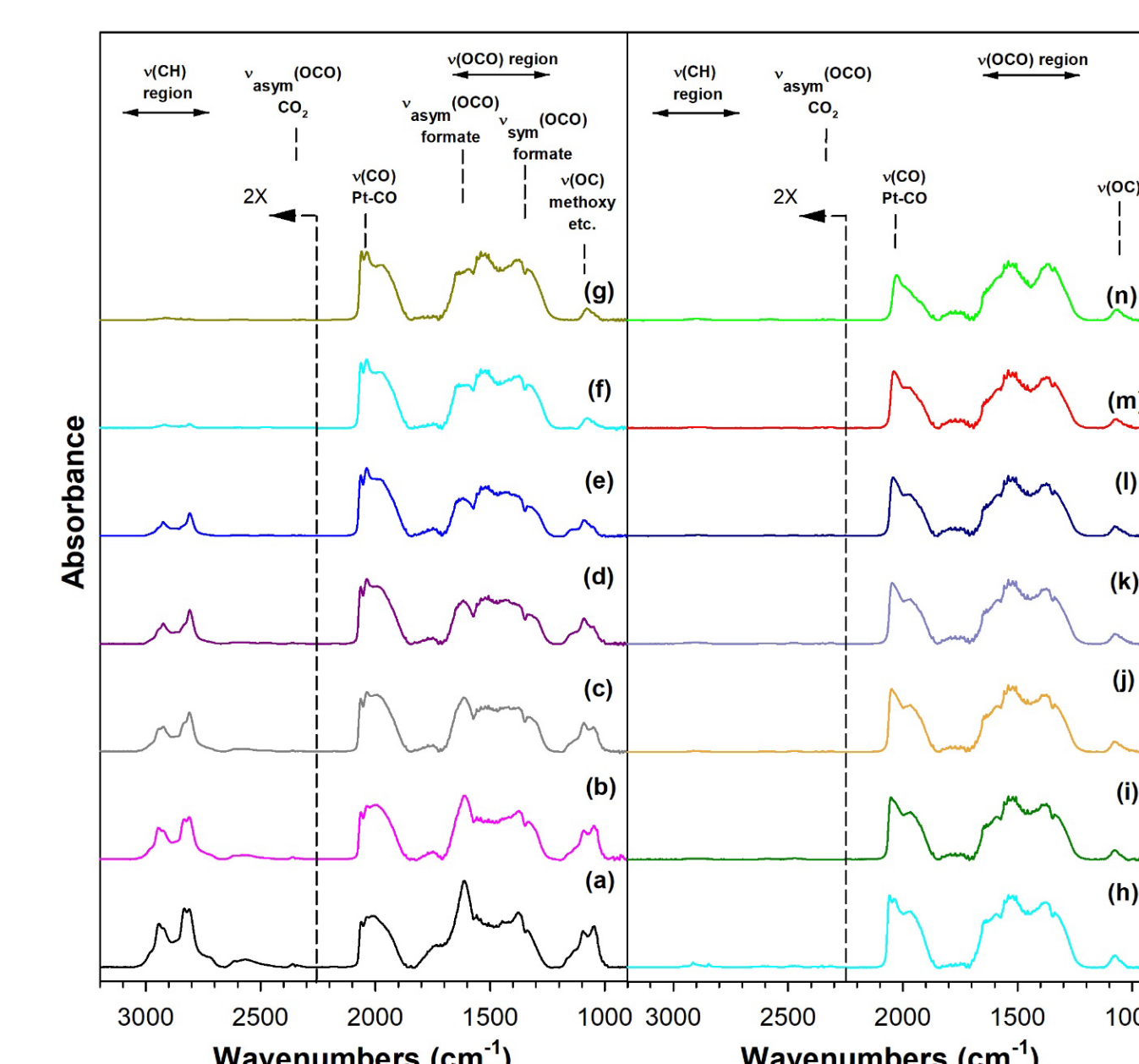


Figure 2: DRIFTS of (a) adsorbed methanol at 50°C, and temperature stepped steam reforming of adsorbed methanol in 30 cm³/min of 4.4% H₂O (balance He) over 0.54%Li-2%Pt/m-ZrO₂ at (a) 50°C, (b) 75°C, (c) 100°C, (d) 125°C, (e) 150°C, (f) 175°C, (g) 200°C, (h) 225°C, (i) 250°C, (j) 275°C, (k) 300°C, (l) 325°C, (m) 350°C, and (n) 350°C (He purge for 10 min).

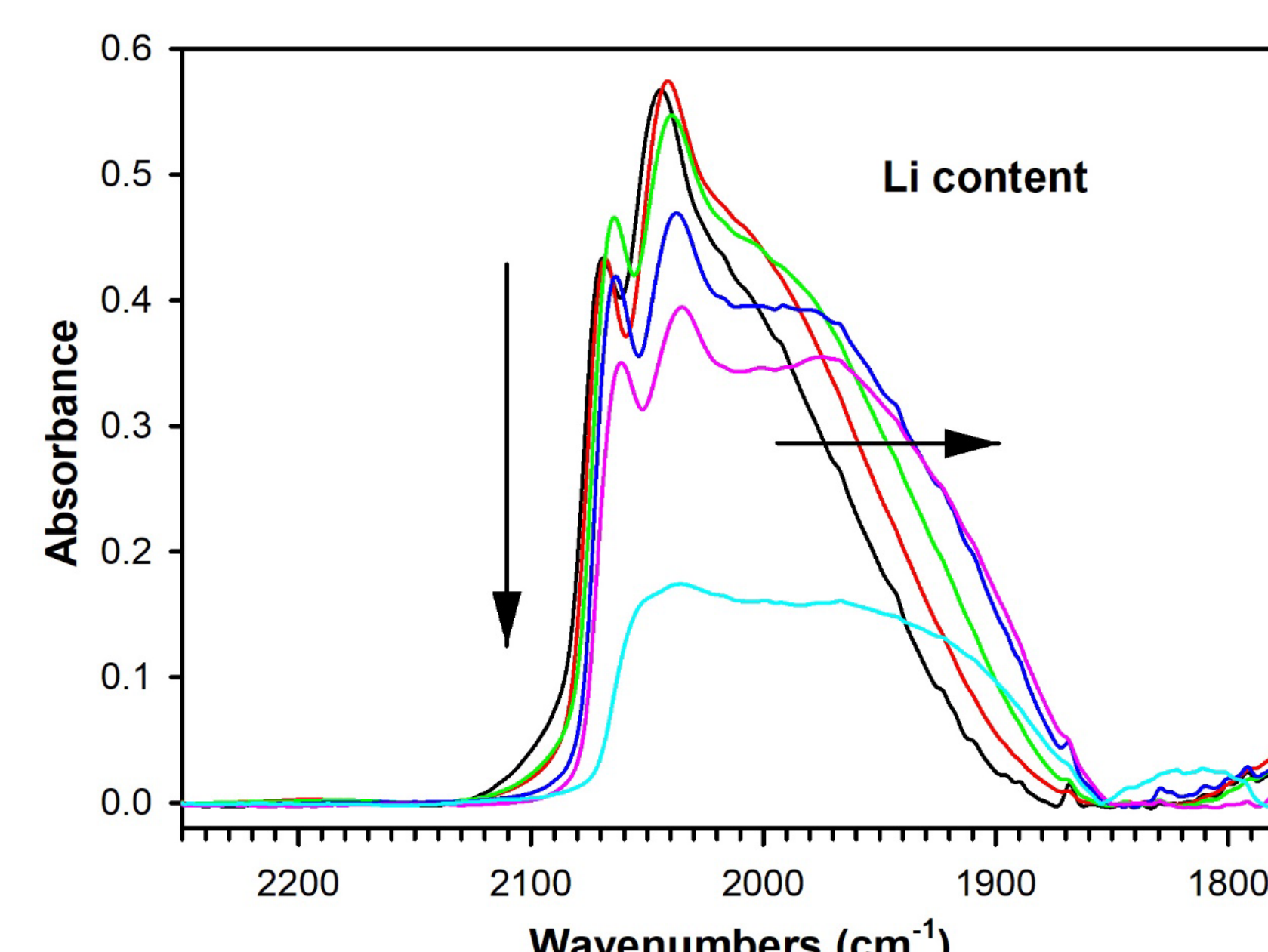


Figure 4: DRIFTS of the Pt carbonyl ν(CO) stretching region at 150°C during transient steam reforming of methanol, including (black) unpromoted 2%Pt/m-ZrO₂, and the same promoted with (red) 0.15% Li, (green) 0.30%Li, (blue) 0.54%Li, (pink) 0.75%Li, (cyan) 1.5%Li.

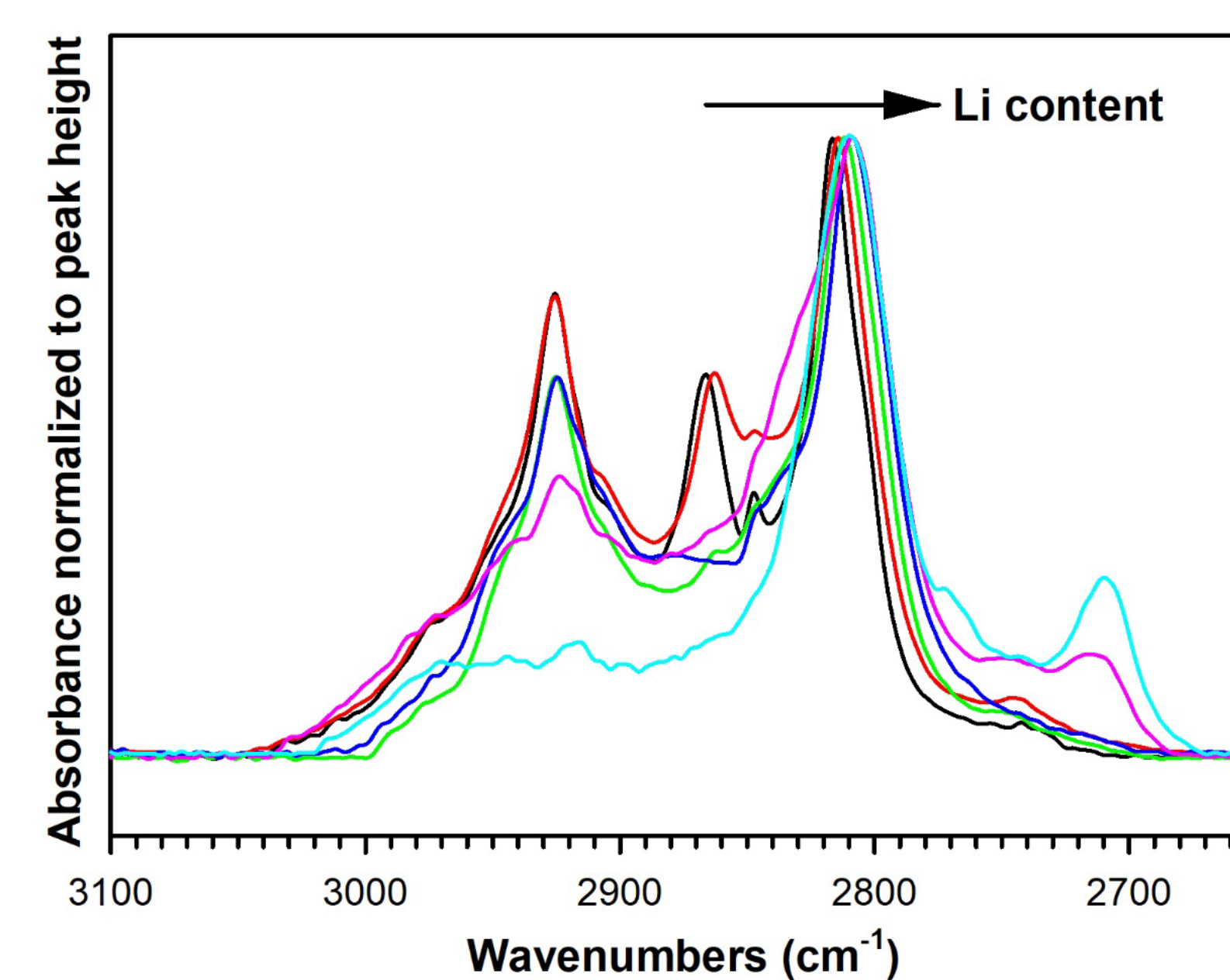


Figure 6: DRIFTS of the formate ν(CH) stretching region at 150°C during transient steam reforming of methanol, including (black) unpromoted 2%Pt/m-ZrO₂, and the same promoted with (red) 0.15% Li, (green) 0.30%Li, (blue) 0.54%Li, (pink) 0.75%Li, (cyan) 1.5%Li. Note that spectra are normalized by peak height to emphasize peak displacements.

Observations and Conclusions

- In temperature programmed reaction of methanol steam reforming, all catalysts showed some formaldehyde formation at low temperature, suggesting adsorbed formaldehyde is a likely intermediate during methanol steam reforming, formed from the dehydrogenation of methoxy species. For the catalyst having no Li, a significant route is that the formaldehyde decomposes to CO and H₂, which is the unselective pathway. With increasing the Li loading, the H₂ peak increases systematically and the CO peak decreases systematically. Moreover, formaldehyde evolution increases. This suggests one of two pathways. First, formaldehyde formed from dehydrogenation of methoxy species undergoes oxidation to formate species, which releases H₂. Formate then undergoes forward decomposition (catalyzed by co-adsorbed H₂O) to H₂ and CO₂. The second possibility is CO produced from formaldehyde decomposition undergoes water-gas shift through formate intermediate species. The proposed mechanism can be seen in figure 7 below.

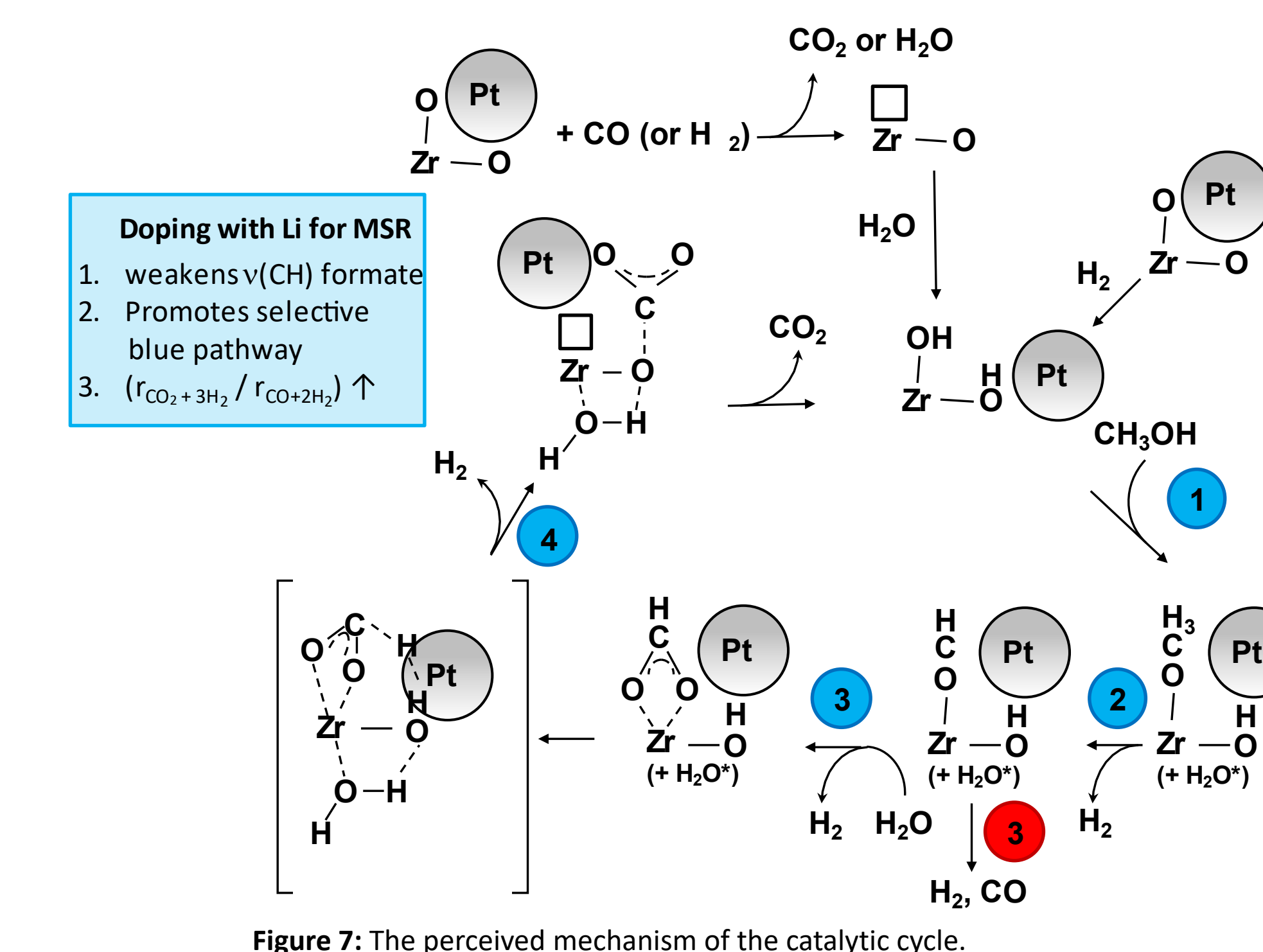


Figure 7: The perceived mechanism of the catalytic cycle.

By looking at the DRIFTS Figures

- Adsorbing methanol at 50 °C, methoxy species are formed, as the ν(CO) stretching bands are observed in the 1000 to 1200 cm⁻¹ region. These include Type I at higher wavenumber and Type II (defect-associated with more coordinative unsaturation) at lower wavenumbers. Methoxy species are converted to formate, and formate bands already begin to form at 50 °C. With increasing temperature, formate species are converted to carbonate species. With increasing Li loading, the formate species are converted more rapidly to carbonates, as the C-H bond is weakened; the ν(CH) band moves to lower wavenumbers. We believe that this is caused by increased basicity causing the -OOC functional group of the formate molecule to interact more strongly with the catalyst surface, which in turn weakens the formate C-H bond. In addition to these observations, the Pt-carbonyl band intensity is attenuated by adding Li, suggesting some direct contact of Li with Pt surfaces.
- From what I learned through the research project is that the optimum lithium percentage is between 0.54% and 0.75%. These percentages show the best proportions of carbon monoxide and hydrogen selectivity and having carbon dioxide be evolved at relatively low temperatures. This is seen in the MS signal graphs in Figure 5.
- The reason the loading percentages cannot go any higher is due to the CO₂ association being too strong at higher alkali presences since it is an acidic molecule. This in turn diminishes the activity due to product inhibition, as evidenced by the high temperature CO₂ desorption peak at 1.5%Li loading.

References

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3. Rajabi, Zahra et al. "Low Temperature Ethanol Steam Reforming: Selectivity Control with Lithium Doping of Pt/M-ZrO₂." *Catalysis Today*, vol. 402, 2022, pp. 335-349, doi:<https://doi.org/10.1016/j.cattod.2022.06.018>.
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- The catalyst surface was saturated by injecting methanol and then purging in argon for 15 min to remove weakly bound species. The catalyst was then heated to 800 °C and the MS signals of H₂, CO, CO₂, and formaldehyde were followed in order to steps involved in converting methanol by steam, as well as the effect of Li promoter loading.