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Abstract

Hydrogen as a green energy resource is regenerable and more desirable as there are increasing demands regarding sustainable energy and environmental protection. Harvesting hydrogen efficiently through ethanol steam reforming by promoting cesium to platinum-zirconia catalyst is investigated by spectroscopic techniques.

Background

One step in hydrogen production is the water-gas shift reaction, which is reversible and exothermic. Water-gas shift may be conducted either with or without a heterogeneous catalyst. In prior research, Honda and Symyx discovered that adding an alkali promoter to a catalyst consisting of zirconia supported platinum nanoparticles lowered the activation energy. Honda and UK-CAER researchers found that this was due to weakening of the C-H bond of the formate intermediate.



The goal is to investigate a possible electronic effect of catalysts containing Cs as a promoter in ethanol steam reforming, where C-C bond breaking of the acetate intermediate is expected to be analogous to the C-H bond breaking in WGS. This is anticipated to result in an increase in the H₂ selectivity.

HYPOTHESIS

- Cs addition to Pt/ZrO₂ is proposed to weaken the C-C bond of the acetate intermediate in ESR and lower the activation energy barrier of this elementary step.
- This is anticipated to promote the decarboxylation/demethanation pathway resulting in higher selectivity: $CH_3COOH^* + 2H_2O \rightleftharpoons CH_4 + CO_2 + 2H_2O \rightleftharpoons 4H_2 + CO_2$ versus the undesired decarbonylation pathway: $CH_3COOH^* \rightleftharpoons 2CO + 2H_2$ (* adsorbed species)

Methodology

- Incipient wetness impregnation (IWI) technique was used to prepare catalysts. Unpromoted and cesium-doped 2%Pt/m-ZrO₂ catalysts were prepared with diverse loadings (0.72%, 1.45%, 2.17%, 2.89%, 3.87%, 4.80%, 5.78%, 7.22%, 10.41% or 14.45% by weight) of Cs. Monoclinic phase zirconia was impregnated with 2% Pt using aqueous Pt(NH₃)₄(NO₃)₂. Catalysts were separated and promoted using an aqueous solution of Cs(NO₃) after calcination. Catalysts were dried and re-calcined after impregnation of the cesium dopant.
- Catalysts were characterized using temperature programmed reduction (TPR), TPR with mass spectrometry (MS), *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and temperature programmed desorption with MS.

Results

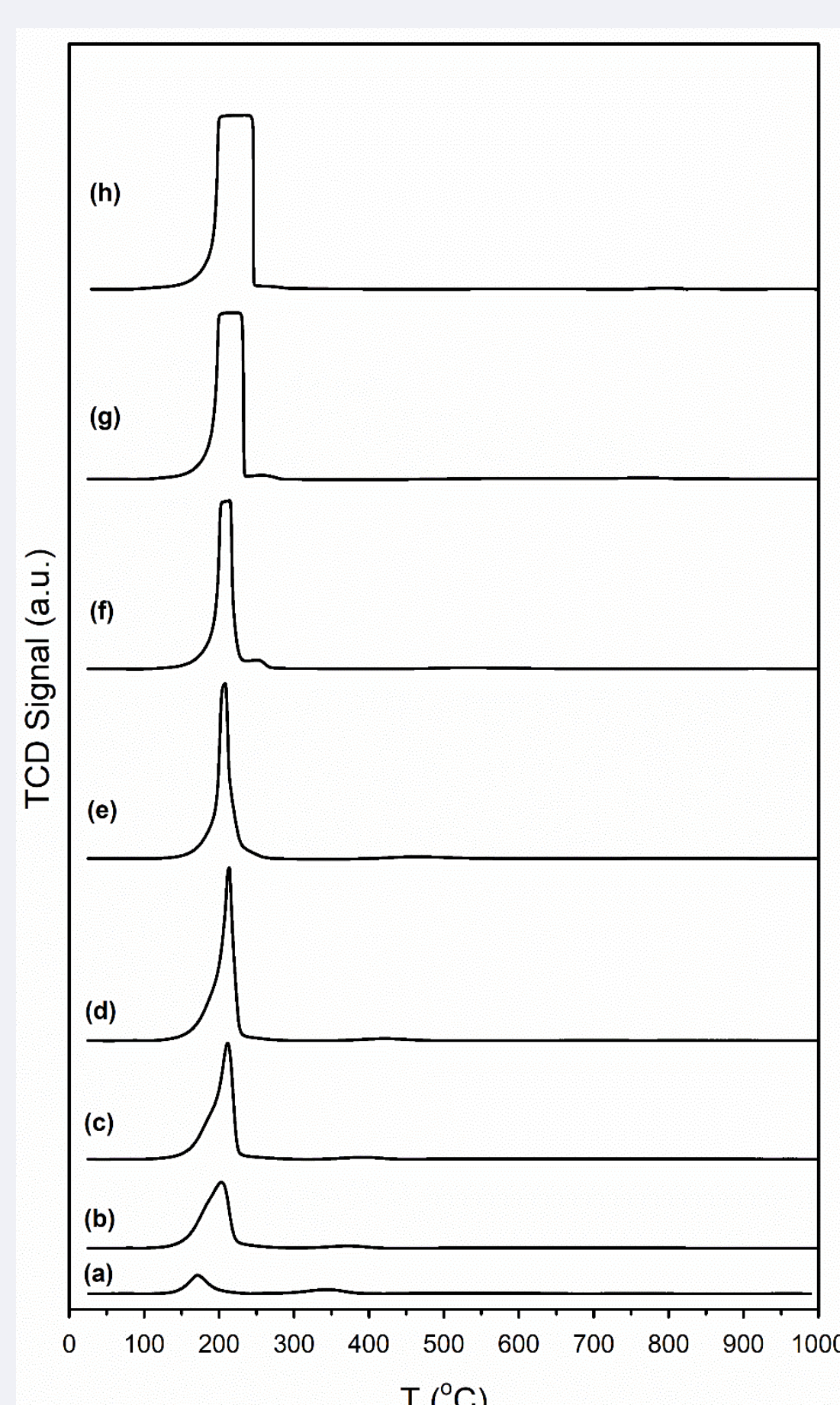


Figure 1. TPR profiles of (a) 2%Pt/ZrO₂, (b) 2.89%Cs-2%Pt/ZrO₂, (c) 3.87%Cs-2%Pt/ZrO₂, (d) 4.80%Cs-2%Pt/ZrO₂, (e) 5.78%Cs-2%Pt/ZrO₂, (f) 7.22%Cs-2%Pt/ZrO₂, (g) 10.41%Cs-2%Pt/ZrO₂ and (h) 14.45%Cs-2%Pt/ZrO₂.

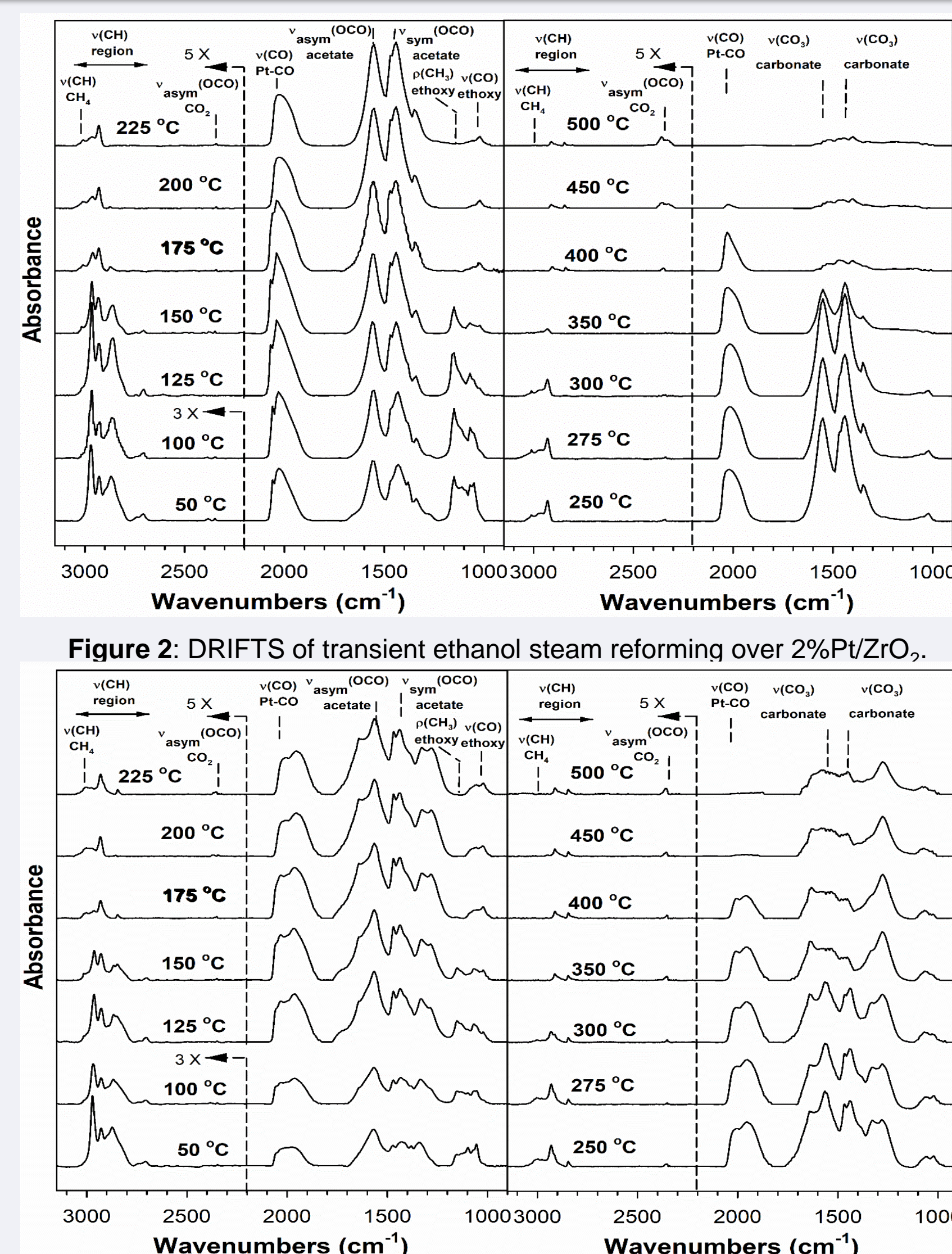


Figure 2. DRIFTS of transient ethanol steam reforming over 2%Pt/ZrO₂.

Figure 3. DRIFTS of transient ethanol steam reforming over 2.89%Cs-2%Pt/ZrO₂.

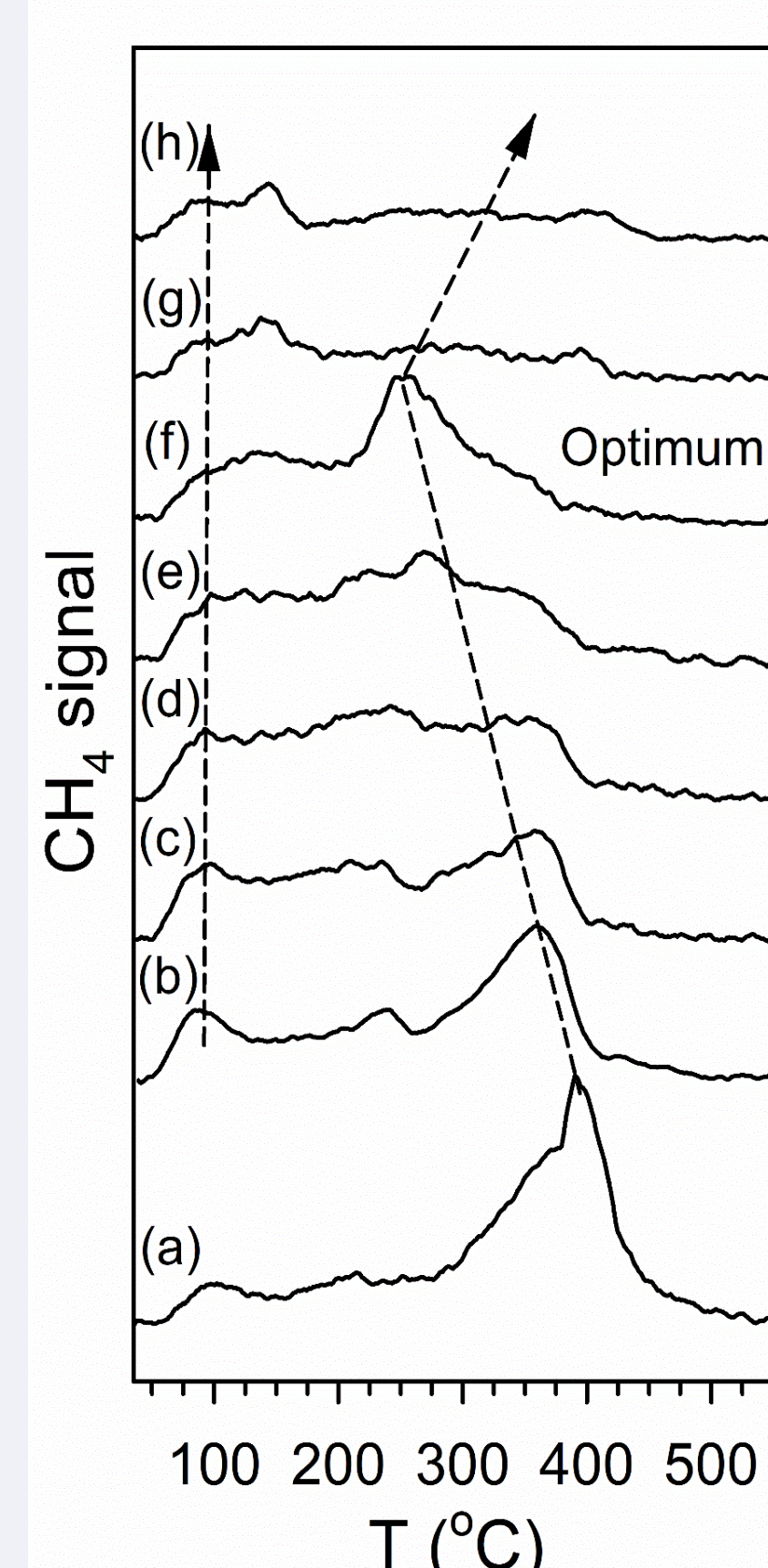


Figure 4. TP-reaction-MS of ethanol steam reforming over (a) 2%Pt/ZrO₂, (b) 2.89%Cs-2%Pt/ZrO₂, (c) 3.87%Cs-2%Pt/ZrO₂, (d) 4.80%Cs-2%Pt/ZrO₂, (e) 5.78%Cs-2%Pt/ZrO₂, (f) 7.22%Cs-2%Pt/ZrO₂, (g) 10.41%Cs-2%Pt/ZrO₂ and (h) 14.45%Cs-2%Pt/ZrO₂.

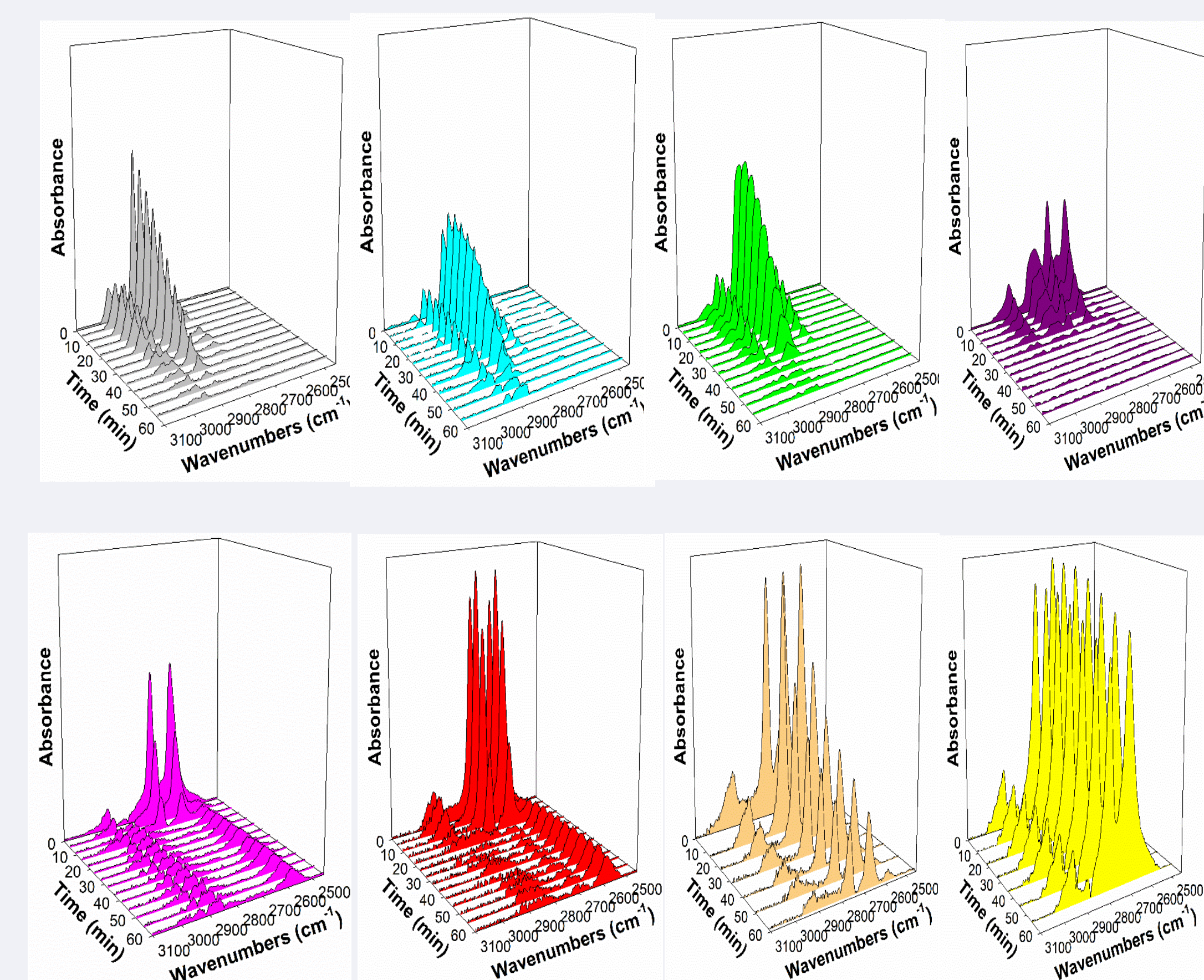


Figure 5. Formate decomposition in steam at 130°C, including (gray) 2%Pt/ZrO₂, (cyan) 2.89%Cs-2%Pt/ZrO₂, (green) 3.87%Cs-2%Pt/ZrO₂, (purple) 4.80%Cs-2%Pt/ZrO₂, (pink) 5.78%Cs-2%Pt/ZrO₂, (red) 7.22%Cs-2%Pt/ZrO₂, (orange) 10.41%Cs-2%Pt/ZrO₂, and (yellow) 14.45%Cs-2%Pt/ZrO₂.

Figure 1 shows activation of the catalyst in H₂, which forms reduced defects in zirconia (evolving CO_x as surface carbonates decompose) and reduces Pt oxide to Pt metal nanoparticles. The shift in the peaks to higher temperature indicates that Cs tends to hinder the activation process. Figures 2 and 3 show the different species that form during ESR by doing a temperature stepped reaction. At low T, ethoxy species form that convert to acetate by 175°C. Forward acetate decomposition to CH₄ and CO₂ is promoted by Cs, as the T for the gas phase CH₄ band (3010 – 3020 cm⁻¹) appears starting at 125°C versus 150°C for the unpromoted catalyst. A shift to lower T for acetate decomposition in steam was also observed in temperature programmed reaction with mass spectrometry (Figure 4). Figure 5 shows the promoting effect of Cs in the analogous water-gas shift reaction, where a red-shift in the C-H band is observed and formate decomposes faster. Excessive Cs blocks active sites and then hinders the reaction.

Summary

Zirconia was doped with various loadings of Cs. Cs was found to weaken the C-H bond of formate in WGS and, in an analogous manner, the C-C bond of the acetate intermediate in ethanol steam reforming. This increases the selectivity to the desired decarboxylation/demethanation pathway over the decarbonylation pathway. As a result, including the steam reforming of methane, the overall H₂ selectivity of the steam reforming process may be improved.

Acknowledgments

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References

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