

Facilitating C-C Bond Scission by Alkali Doping of Pt-ZrO₂ Catalyst for ESR

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ABSTRACT

Due to recent, rapid increases in the consumption of energy, there is an incredible demand for clean and efficient fuel. Hydrogen is a promising carrier for energy since it has the unique property that oxidizing it produces only water (steam) as a product. Ethanol steam reforming (ESR) is the process of converting ethanol and water to carbon dioxide and hydrogen, typically via a metal oxide catalyst. In my project, sodium doped platinum-zirconia catalyst (2.5%Na-2%Pt/m-ZrO₂) was compared to undoped platinum-zirconia catalyst (2%Pt/m-ZrO₂) via Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) in order to compare the strength of the acetate C-C bond vital to the catalytic cycle of ESR. It was found that the promoted catalyst cleaved this bond at lower temperatures than the unpromoted catalyst, indicating that the promoted catalyst has the potential to improve ESR reaction rates.

BACKGROUND

Fuel cells offer an attractive means of eliminating line sources of emissions from vehicles and forms of portable power. However, current costs of fuel cells and hydrogen production are too high for these fuel cells to be currently feasible. Methanol steam reforming (MSR) and ESR are two promising pathways to produce this hydrogen. Previous work showed that alkali doping of catalysts improved the rate of formate decomposition in Methanol Steam Reforming (MSR).¹ In my project, I tested whether sodium doping of a Pt-ZrO₂ catalyst would improve the analogous rate of acetate decomposition in ESR.

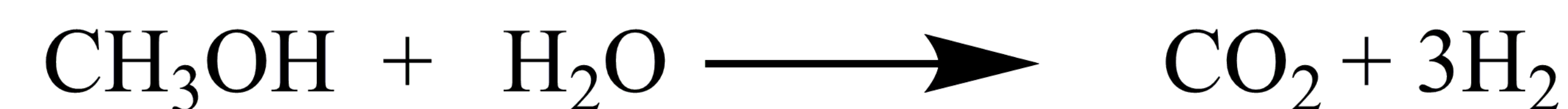
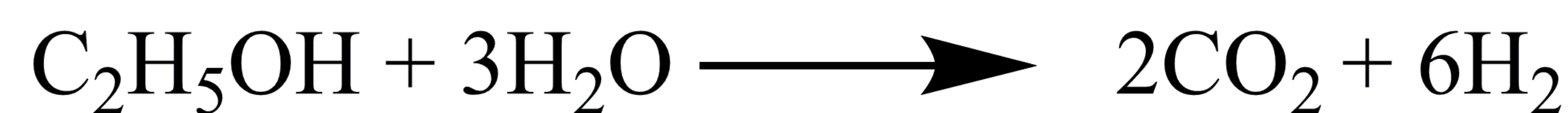


Fig. 1: Overall reaction for (top) Ethanol Steam Reforming and (bottom) Methanol Steam Reforming

HYPOTHESIS

By sodium doping the Pt-ZrO₂ catalyst, we expect to see a weakening of the C-C bond of acetate in ESR and the analogous C-H bond in MSR.

METHODOLOGY

Catalyst Preparation: Monoclinic zirconia support was obtained and sieved to the proper size. Platinum was added to the support by the incipient wetness impregnation (IWI) technique using an aqueous solution of tetraamineplatinum(II) nitrate. After impregnation of platinum, the sample was dried and calcined. Sodium was then added by IWI using an aqueous solution of sodium nitrate. After impregnation of sodium, the sample was again dried and calcined.

Data Collection: Data was collected using DRIFTS and temperature programmed desorption (TPD) combined with Mass Spectrometry (MS). DRIFTS was conducted using 100 sccm steam following ethanol, methanol, acetic acid, or formic acid adsorption. CH₄ peaks evolved at 210°C (minor) and 400°C (major) for undoped catalyst and at 150°C (major), 275°C (major) and 360°C (minor) for Na doped catalyst.

RESULTS

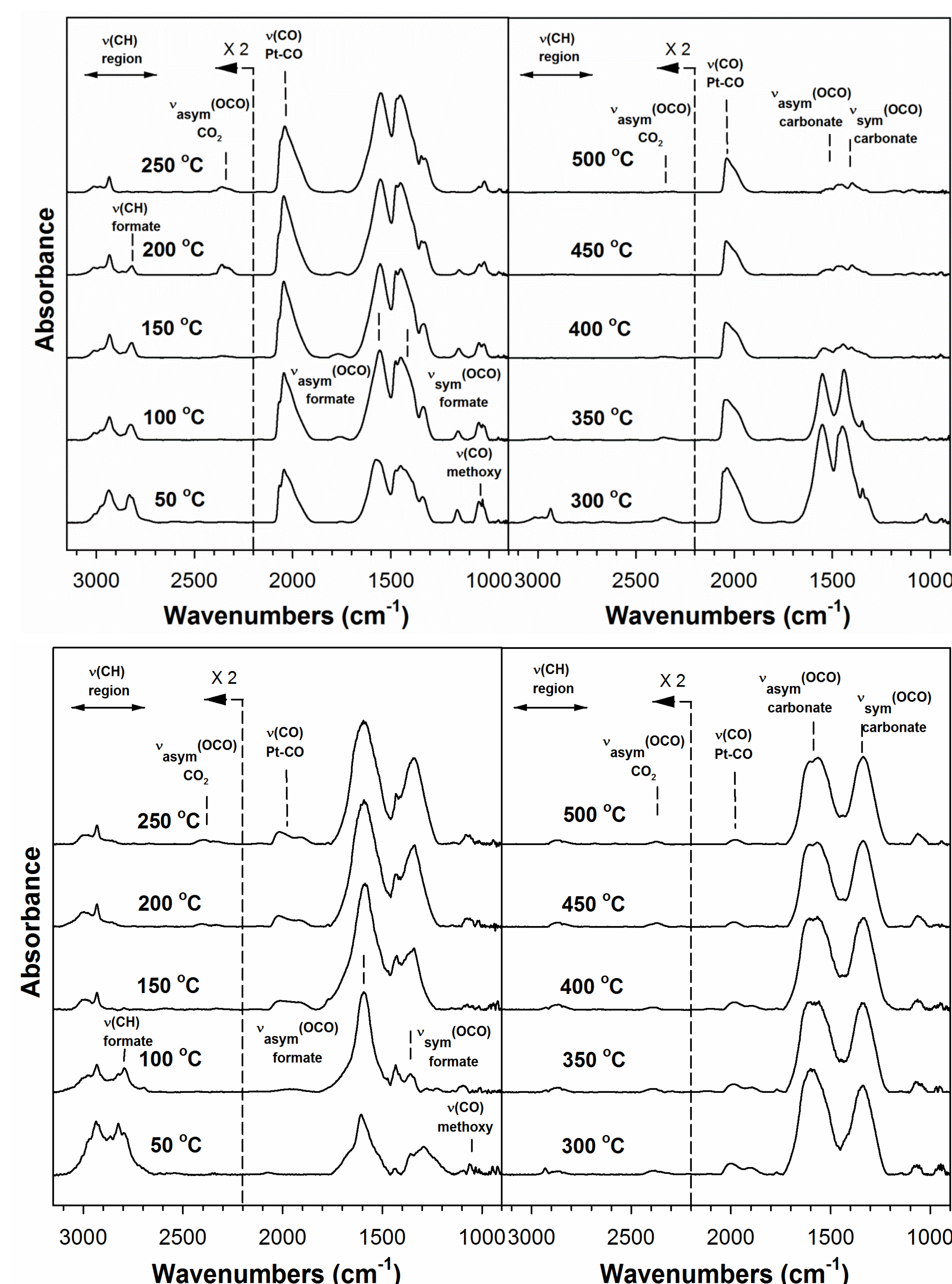


Fig. 2: In-situ DRIFTS spectra of transient MSR using 100 sccm of steam following adsorption of methanol for (top) 2%Pt/m-ZrO₂ and (bottom) 2.5%Na/2%Pt/m-ZrO₂.

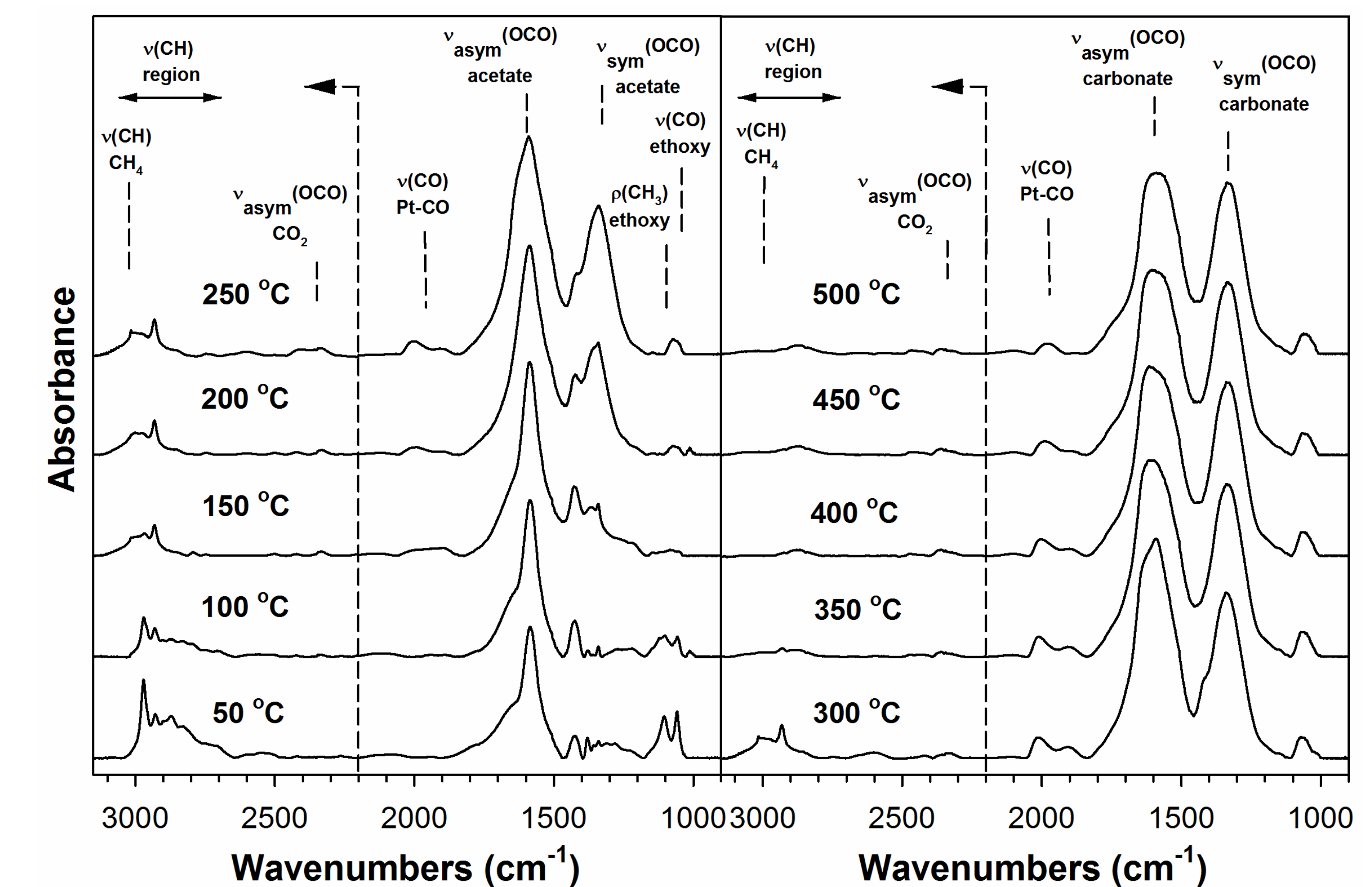
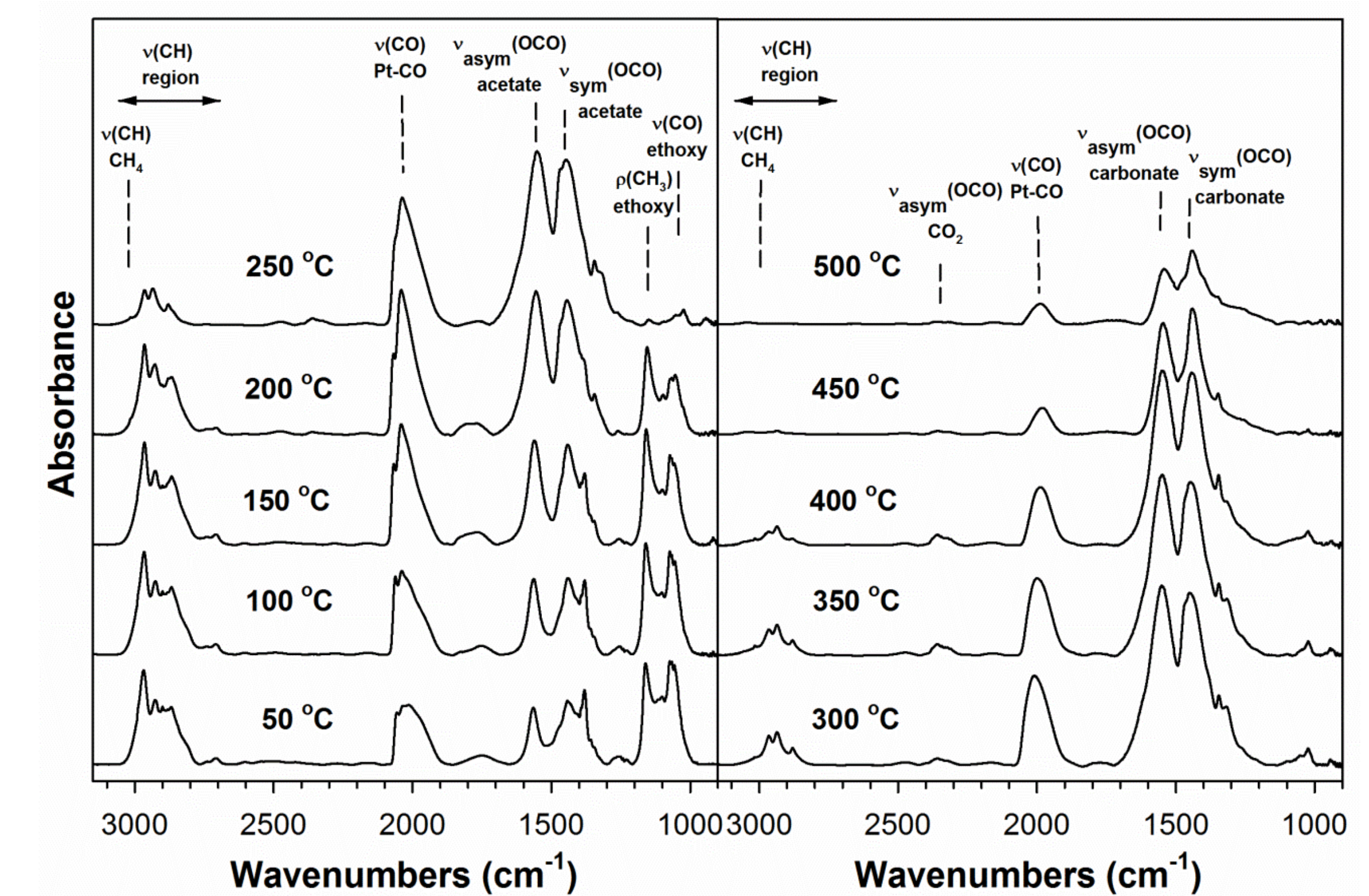


Fig. 3: In-situ DRIFTS spectra of transient ESR using 100 sccm of steam following adsorption of ethanol for (top) 2%Pt/m-ZrO₂ and (bottom) 2.5%Na/2%Pt/m-ZrO₂.

SUMMARY

- ❖ Na doping of Pt/ZrO₂ increases the basicity of the catalyst.
- ❖ C-C scission of acetate intermediate occurs at lower T in DRIFTS and TPD-MS experiments, with CH₄ evolving at lower T.

REFERENCES

1. Martinelli, M., Jacobs, G., Graham, U.M., Davis, B.H., "Methanol steam reforming: Na doping of Pt/YSZ provides fine tuning of selectivity," Catalysts 7 (2017) 148. <https://doi.org/10.3390/catal7050148>