

The role of different supports for low temperature plasma assisted CO₂ methanation

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Abstract: In this contribution, we report the plasma catalytic CO₂ methanation activities on Ni supported on Al₂O₃, ZrO_x, BaTiO₃, commercial CeO₂ and a CSIRO catalyst. Meanwhile we studied surface chemistry under plasma conditions by using a self-designed in-situ plasma DRFIT. Our finding suggests the basicity nature of the support plays significant role in tuning surface adsorbed species during the plasma reaction process.

1. Introduction

Conventional CO₂ hydrogenation is through thermal chemical pathway, which is constrained by kinetic and thermodynamic limitations and requires high pressure and temperatures. It not only consumes energy for compression and heating but also leads to lengthy ramping up and down step which further consumes lead power. Lowering reaction temperature has been attempted by the research community but often results in lower conversion, which means further post-reaction processing to increase the product purity, inevitably increasing the production cost and carbon intensity. Non-thermal plasma (NTP), also known as cold plasma, produces highly energetic electrons (1–10 eV) that collide with gas molecules to produce highly reactive species (i.e., ions, radicals, excited atoms and molecules), enabling kinetically or thermodynamically unfavoured reactions at low temperatures. In recent years, researchers have found if an effective catalyst is used in the NTP process, it not only promotes reactant dissociation at low temperature on the catalyst surface but also facilitates high product selectivity.

2. Methods

Catalytic testing was conducted in a lab designed rig. In-situ diffuse reflectance infrared Fourier transform spectroscopy (In-situ DRIFTS) was measured on a self-designed plasma incorporated DRFIT. coupled with Mass spectroscopy and plasma. TPD-CO₂, TPR, XRD, XPS and other routine analysis were conducted as usual.

3. Results and Discussion

Figure 1 presents a representative in-situ DRFIT spectra obtained with time on stream after plasma is turned on for a CSIRO catalyst. It was observed that as soon as plasma is turned on, adsorbed bicarbonate (HCO₃), Bid-CO₃²⁻ species started appearing. With time progressing, some of the bicarbonate peaks disappeared while Bid-CO₃²⁻ peak strengthened and at the same time, HCO, CH₃O peaks' strength increased with time. No adsorbed CH₄ peak was observed during the whole reaction process. However, mass spectra results indicated CH₄ presence in the product,

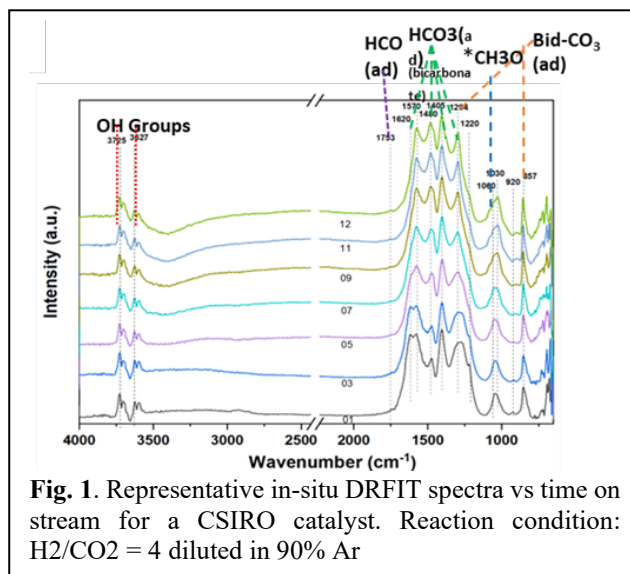


Fig. 1. Representative in-situ DRFIT spectra vs time on stream for a CSIRO catalyst. Reaction condition: H₂/CO₂ = 4 diluted in 90% Ar

suggesting CH₄ species was quickly desorbed from the surface once formed and no formate species were observed.

However, these observations are unique to the CSIRO catalyst. The DRIFT spectra for all other catalysts on different support were different, which was believed to be associated with the surface properties of the catalysts.

4. Conclusion

In-situ plasma DRIFT results helped significantly in understanding the surface chemistry under plasma reactions. The weak, medium strength and strong basicity of the surface played a significant role in forming adsorbed surface species, which led to different reaction pathways.

Acknowledgement

Authors thank Prof Xiaolei Fan from Manchester University and Prof Huanhao Chen from Nanjin Tech University for collaboration on Plasma DRFIT setup and thank CSIRO Research Office for Funding.

References

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