



## 16<sup>th</sup> INTERNATIONAL CONFERENCE ON CARBON DIOXIDE UTILIZATION

# Catalytic conversion of CO<sub>2</sub> to syngas using a crystalline metal oxide

Mina Zarabian,<sup>a\*</sup> Azfar Hassan,<sup>a</sup> Venkataraman Thangadurai,<sup>b</sup> Pedro Pereira-Almao<sup>a</sup>

<sup>a</sup>Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive NW, Calgary, AB, T2N-1N4, Canada

<sup>b</sup>Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, AB, T2N-1N4, Canada

\*Corresponding author: mzarabia@ucalgary.ca

Keywords: dry reforming of methane, syngas, metal oxide

Hydrocarbons can be converted to hydrogen, as a value added product, through reforming processes including steam reforming, partial oxidation, and dry reforming. Among these techniques, dry reforming of methane (DRM) has gained considerable attention due to the fact that it not only gives rise to the formation of syngas but also contributes to CO<sub>2</sub> mitigation

Extensive industrial application of DRM has been hindered by the highly endothermic nature of the reaction and quick deactivation of the catalysts [1, 2]. Most studied catalysts for this process thus far are based on transition metals (Ni, Fe, Co) loaded on ceramic supports (Al<sub>2</sub>O<sub>3</sub>, ZrO, and La<sub>2</sub>O<sub>3</sub>). The metal surface acts as active site to dissociate methane into carbon and H<sub>2</sub>, this atomic carbon is very reactive and mostly gasifies with CO<sub>2</sub> or H<sub>2</sub>O; however, some of it transforms into inactive carbon and dissolves in the metal bulk, forming a solid solution. When the amount of dissolved carbon reaches the solubility limit, phase separation happens and carbon starts growing as a whisker on the surface of metal, and thus deactivates the catalyst. We herein report on a crystalline metal oxides, which activate methane and carbon dioxide below 600 °C. This material is based on solid crystalline materials in which active sites are highly mobile and distributed in three dimensions.

We studied an alternate adsorption of the reactants as well as the mixture of CO<sub>2</sub> and CH<sub>4</sub> on the catalyst, a procedure evidencing individual

activation of CH<sub>4</sub> and CO<sub>2</sub>. Following the evolution of gases with a Quadrupole Mass Spectrometer (QMS) allowed identifying that CH<sub>4</sub> dissociation evolves di-hydrogen and CO and traces of water production. The catalyst seem to provide oxygen for CO and H<sub>2</sub>O release, at least partly cleaning the surface from carbenes left by the dissociative adsorption of methane. All products decreased to a constant level when the catalyst did not have more oxygen atoms to donate or there was no more sites for chemisorption of methane. At this stage, the gas was switched to pure CO<sub>2</sub>, the probable deposited carbene species on the surface of the solid react with CO<sub>2</sub>, the lost oxygen atoms in the catalyst were again recovered via reinsertion on the solid vacancies and all the products for dry reforming retrieved. This crystalline oxide developed withstands high temperature and no effect on coking deactivation is observed over 24 hr dry reforming of methane.

### References

- [1] K. Mondal, S. Sasmal, S. Badgandi, D. R. Chowdhury, and V. Nair, "Dry reforming of methane to syngas: a potential alternative process for value added chemicals—a techno-economic perspective," *Environmental Science and Pollution Research*, pp. 1-7, 2016.
- [2] D. Pakhare and J. Spivey, "A review of dry (CO<sub>2</sub>) reforming of methane over noble metal catalysts," *Chemical Society Reviews*, vol. 43, pp. 7813-7837, 2014.
- [3] C.-j. Liu, J. Ye, J. Jiang, and Y. Pan, "Progresses in the Preparation of Coke Resistant Ni-based Catalyst for Steam and CO<sub>2</sub> Reforming of Methane," *ChemCatChem*, vol. 3, pp. 529-541, 2011.