



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

# Alkaline Zirconate Catalysts for CO<sub>2</sub> Storage and H<sub>2</sub> Production through CH<sub>4</sub> Dry Reforming

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In recent decades, CH<sub>4</sub> and CO<sub>2</sub> emissions have been responsible for climate change and global warming, as both gases are the major contributors to the greenhouse effect.<sup>[1]</sup> One option for limiting this effect is to reduce the emission of both gases by converting them into an alternative and cleaner energy source, such as H<sub>2</sub>.<sup>[2]</sup> Among H<sub>2</sub> production processes, the most commonly used is CH<sub>4</sub> dry reforming.<sup>[3]</sup>

Li and Na zirconates (Li<sub>2</sub>ZrO<sub>3</sub> and Na<sub>2</sub>ZrO<sub>3</sub>) were synthesized and characterized by powder XRD, SEM and N<sub>2</sub> physisorption. All materials were tested for CO<sub>2</sub> capture (TGA), desorption processes (TPD) and CH<sub>4</sub> dry reforming (MDR, catalytic tests). In this work a consecutive process is proposed in order to produce H<sub>2</sub>: a carbonation step followed by a catalytic stage under CH<sub>4</sub> atmosphere. Two effects were evaluated: i) the addition of NiO (between 2.5 and 10 wt%) on Na<sub>2</sub>ZrO<sub>3</sub> and ii) the modification of the carbonation atmosphere.

In the first part, all samples showed a slight inhibition for CO<sub>2</sub> capture due to the presence of NiO, which partially blocked superficial active sites where CO<sub>2</sub> can be chemisorbed. Then in catalytic tests, NiO addition resulted in greater production of H<sub>2</sub> than that of pure Na<sub>2</sub>ZrO<sub>3</sub>, followed by a drastic reduction in the reaction temperature; especially for NiO-doped Na<sub>2</sub>ZrO<sub>3</sub> sample containing 10 wt% of NiO. Additionally, regeneration and cyclic behavior showed that it is possible to accomplish consecutive cycles of CO<sub>2</sub> capture-MDR with a considerable Na<sub>2</sub>ZrO<sub>3</sub> regeneration.

In the second part, it was observed that lithium and sodium zirconates are able to capture CO<sub>2</sub>, being Na<sub>2</sub>ZrO<sub>3</sub> the sample with the best performance in all the atmospheres tested (CO<sub>2</sub>, CO and CO+O<sub>2</sub>). In

the CO cases, it was observed that CO oxidation proceeds first, producing CO<sub>2</sub> that is subsequently chemisorbed. These carbonated materials were used as CO<sub>2</sub> sources during MDR reaction (Figure 1). Results showed that in both samples, the highest amount of H<sub>2</sub> (~30%) was produced when CO+O<sub>2</sub> atmosphere was used during carbonated stage. Hence, it was established that alkaline zirconates can be used as bifunctional materials as: i) CO<sub>2</sub> captors and then as ii) catalytic materials in MDR.

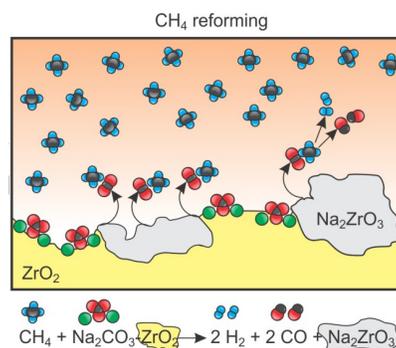


Figure 1. MDR over a carbonated-Na<sub>2</sub>ZrO<sub>3</sub> catalyst.

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### References

- [1] S.J. Chapman, M. Thurlow, The influence of climate on CO<sub>2</sub> and CH<sub>4</sub> emissions from organic soils, *Agric. For. Meteorol.* 1996, 79, 205.
- [2] J. Holladay, J. Hu, D. King, Y. Wang, An overview of H<sub>2</sub> production technologies, *Catal. Today.* 2009, 139, 244.
- [3] A. Wolfbeisser, O. Sophiphun, J. Bernardi, J. Wittayakun, K. Föttinger, G. Rupprechter, Methane dry reforming over ceria-zirconia supported Ni catalysts, *Catal. Today.* 2016, 277, 234.