

## Methanol steam reforming on Pd and Zn substituted LaCoO<sub>3</sub>

J. Kuc<sup>1</sup>, M. Neumann<sup>2</sup>, M. Armbrüster<sup>2</sup>, S. Yoon,<sup>1</sup> A. Weidenkaff,<sup>1</sup> Santhosh Kumar Matam<sup>1\*</sup>  
<sup>1</sup>Empa, Swiss Federal Laboratories for Materials Science and Technology, CH-8600  
 Dübendorf, Switzerland. <sup>2</sup>Max-Planck-Institut für Chemische Physik fester Stoffe, D-01187  
 Dresden, Germany. \*corresponding author: santhosh.matam@empa.ch

### Introduction

Renewable energy has been the topic of intense research in the recent past to deal with energy and environmental issues such as finite fossil fuel reserves and global warming. One of the most promising ways to deal with these issues is fuel cells (FCs) which produce electricity from hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>) and emit only water (H<sub>2</sub>O), meeting the zero emission concept by closing the carbon loop. The high energy density methanol as H<sub>2</sub> carrier is easier and safer to handle as compared to pressurized cylinders. Hence, the steam reforming of methanol (SRM) is attractive to feed on-board FCs with H<sub>2</sub> [1-3]. This project investigates novel multifunctional perovskite-type metal oxides as potential SRM catalysts to produce selectively H<sub>2</sub> and CO<sub>2</sub>.

### Materials and Methods

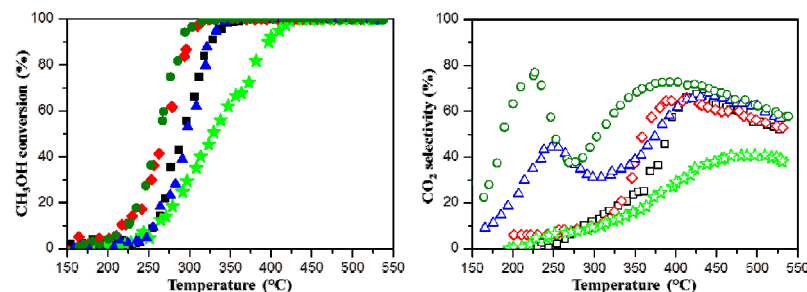
A series of single phase Pd<sup>2+</sup> and Zn<sup>2+</sup>-substituted perovskite catalysts with the general formula of LaCo<sub>1-x</sub>B'<sub>x</sub>O<sub>3-1/2x</sub> (B' = Pd<sup>2+</sup> and Zn<sup>2+</sup>) were prepared by the amorphous citrate method. The as prepared precursors were dried overnight in vacuum at 80 °C and calcined in air at 800 °C (5 °C/min) for 2h (Table 1). The catalysts were thoroughly characterized by various techniques such as N<sub>2</sub>-physisorption, XRD, H<sub>2</sub>-TPR, XPS. The SRM activity of the catalysts was determined in a flow reactor. Various reaction parameters such as feed composition, pretreatment temperature/environment and durability were evaluated.

**Table 1.** Chemical composition and physical properties of the catalysts

Catalysts	Composition (mol%)	Pd wt%	Zn wt%	S <sub>BET</sub> (m <sup>2</sup> /g)
LCO	LaCoO <sub>3-δ</sub>	-	-	9.0
LCPO	LaCo <sub>0.87</sub> Pd <sub>0.13</sub> O <sub>3-δ</sub>	5.3	-	10.6
LCZO	LaCo <sub>0.89</sub> Zn <sub>0.11</sub> O <sub>3-δ</sub>	-	2.9	10.5
LCPZO	LaCo <sub>0.95</sub> Pd <sub>0.025</sub> Zn <sub>0.025</sub> O <sub>3-δ</sub>	1.1	0.66	8.0
LCPZO-1	LaCo <sub>0.75</sub> Pd <sub>0.125</sub> Zn <sub>0.125</sub> O <sub>3-δ</sub>	5.3	3.24	7.0

### Results and Discussion

The catalysts reported in Table 1 show a single phase rhombohedral perovskite structure with the R<sub>3</sub>C space group as evident from XRD indicating that the perovskite structure of LaCoO<sub>3</sub> is retained even after partial substitution of Co with Pd and Zn cations. This holds up to a substitution level of  $x \approx 0.24$  mol%. In situ XRD during reduction and the corresponding H<sub>2</sub>-TPR data show that the reducibility of the catalysts increases with increasing Pd content in the perovskite, which can be attributed to the hydrogen spillover effect. Conversely, the reducibility of LaCoO<sub>3</sub> decreases when only Zn is substituted. The catalyst composition and its reducibility are reflected on the SRM performance (Fig. 1).



**Figure 1.** SRM performance of LaCO (■,□), LCPO (◆,◇), LCZO (star), LCPZO (▲,△) and LCPZO-1 (●,○). Conditions: 3 vol% CH<sub>3</sub>OH, 4 vol% H<sub>2</sub>O at 100 ml/min, catalyst: 100 mg and reductive pre-treatment under 25 vol% H<sub>2</sub> in He at 600°C for 1h.

In general, all the catalysts studied exhibit attractive methanol conversion, except LCZO. However, the catalyst composition determines the CO<sub>2</sub> selectivity, especially below 350°C. Besides CO<sub>2</sub>, CO is the only other by-product detected by GC/MS. Catalysts LCO, LCPO and LCZO show poor CO<sub>2</sub> selectivity. It can be noted that with increasing Pd/Zn molar ratio in the LCO from 0.085 to 1, CO<sub>2</sub> selectivity increases significantly below 350 °C and LCPZO-1 with Pd/Zn molar ratio of 1 presents the best CO<sub>2</sub> selectivity of around 80% at 225°C. The improved selectivity of the catalysts is attributed to the formation of ZnPd-like species [3] as evident from XPS data that show the presence of neither oxidic nor metallic Pd species in the catalysts after the reaction or the reductive pre-treatment. Contrarily, PdO is observed in the fresh catalysts after calcination. The peculiar CO<sub>2</sub> selectivity pattern between 150 and 300°C is attributed to an undefined phase appearance/disappearance as evident from in situ XRD. Above 400°C, the CO<sub>2</sub> selectivity is comparable over all the catalysts, except LCZO. In conclusion, Pd/Zn substituted LCO exhibits better SRM activity and CO<sub>2</sub> selectivity than the un-substituted LCO. The CO<sub>2</sub> selectivity strongly depends on the degree of Pd/Zn substitution (see LCZPO and LCZPO-1) and of ZnPd formation.

**Significance:** Substitution of Co with Pd and Zn (1:1 ratio) into LaCoO<sub>3</sub> not only improves the SRM activity but also boosts the CO<sub>2</sub> selectivity (<250°C) by almost 2 orders of magnitude.

### Acknowledgements

The authors thank the Staatssekretariat für Bildung und Forschung (SBF) for financial support (Project no.: C11.0034) within the frame work of COST Action CM0904.

### References

1. Agrell, J.; Boutonnet, M.; Fierro, J.L.G. *Applied Catalysis A: General* **2003**, 253, 213.
2. Palo, D.R.; Dagle, R.A.; Holladay, J.D. *Chemical Reviews* **2007**, 107, 3992.
3. Armbrüster, M.; Behrens, M.; Föttinger, K.; Friedrich, M.; Gaudry, E.; Matam, S.K.; Sharma, H.R. *Catal. Rev. Sci. Eng.* **2013**, 55, 289.