

## **Tuning of Shape, Defects, and Disorder in Lanthanum-Doped Ceria Nanoparticles: Implications for Oxidative Coupling of Methane**

**Fabiane J. Trindade**

Postdoc, Laboratory of Materials for Energy, Center for Engineering, Modeling, and Applied Social Sciences, Federal University of ABC, Santo André-SP, Brazil.

**Sergio Damasceno**

PhD student, Laboratory of Materials for Energy, Center for Engineering, Modeling, and Applied Social Sciences, Federal University of ABC, Santo André-SP, Brazil.

**Daniel Z. Florio**

Professor, Laboratory of Materials for Energy, Center for Engineering, Modeling, and Applied Social Sciences, Federal University of ABC, Santo André-SP, Brazil.

**Fabio Coral Fonseca**

Principal Investigator M2P, Fuel Cell and Hydrogen Center, Nuclear and Energy Research Institute - Sao Paulo, SP, Brazil.

**Andre S. Ferlauto**

Professor, Laboratory of Materials for Energy, Center for Engineering, Modeling, and Applied Social Sciences, Federal University of ABC, Santo André-SP, Brazil.

The instability of petroleum prices and the advancements in extraction technologies of natural gas has increased the interest in the direct conversion of methane to C<sub>2</sub> products via oxidative coupling of methane (OCM) reactions. The design of catalysts by tailoring the structural defects and disorder has a significant impact on their performance. Within this context, in this work, the fine-tuning of oxygen defects in rod-like NPs was performed via La<sup>3+</sup> doping (La<sub>x</sub>Ce<sub>1-x</sub>O<sub>2-1/2</sub>), *x*, in the 10-70 mol% range. The NPs characterization was performed by SEM, HRTEM, XRD, BET and Raman spectroscopy, and the OCM catalytic performance was evaluated at 750 °C. The relative concentration of reagents (CH<sub>4</sub> and O<sub>2</sub>) and products H<sub>2</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> was measured by an online mass spectrometer. XRD and Raman analysis revealed that the CeO<sub>2</sub> fluorite crystalline structure is essentially maintained in the doped nanorods, even for *x* = 0.7. The Raman spectra analysis indicates that La doping results in the formation of extrinsic and intrinsic oxygen defects, which increase proportionally to La concentration. The catalysts showed good performance for OCM with methane conversion up to 32% and C<sub>2</sub> selectivity up to 44% for *x*=0.5. In addition, all catalysts showed high stability within 20h time on stream. The demonstrated structural defect



control on La-doped CeO<sub>2</sub> NPs can provide important insights to improve the performance of OCM reactions.

**Keywords:** doped-CeO<sub>2</sub> NPs, defect engineering, heterogenous catalysis, oxidative coupling of methane, NPs design

**Support/Acknowledgements:** The authors acknowledge the Multiuser Central Facilities (Universidade Federal do ABC), The authors gratefully acknowledge support from the Center for Innovation on New Energies Shell (ANP)/FAPESP(2017/11937-4) and the FAPESP SPRINT project (2019/00776-5). FCF and ASF are fellows of the Brazilian CNPq.