



# IX Workshop on Novel Methods for Electronic Structure Calculations

10<sup>th</sup> – 19<sup>th</sup> November 2021

La Plata – Argentina

## The Nature of the Active Sites on Ni/CeO<sub>2</sub> Catalysts for Methane Conversions: When Theory and Experiment go Hand in Hand

M. VERÓNICA GANDUGLIA-PIROVANO<sup>a</sup>, PABLO LUSTEMBERG<sup>a, b</sup>

<sup>a</sup> *Institute of Catalysis and Petrochemistry, CSIC, Madrid, Spain.*

<sup>b</sup> *Institute of Physics Rosario, CONICET-UNR, Rosario, Santa Fe, Argentina.*

email: vgp@icp.csic.es

Methane (CH<sub>4</sub>) is difficult to convert to upgraded fuels or chemicals because of the strength of the C-H bonds. Its activation and reforming with CO<sub>2</sub> to syngas or with H<sub>2</sub>O to produce hydrogen, as well as its direct oxidation to methanol, is increasingly important because CH<sub>4</sub> is a potent greenhouse gas. Ni at low loadings on CeO<sub>2</sub> are active for CH<sub>4</sub> activation at room-temperature and for these methane conversion reactions [1-3]. Revealing the nature of the active sites in such systems is paramount to a rational design of improved catalysts. Here we show that the most active sites are Ni atoms in clusters at step edges on the CeO<sub>2</sub> surface, with a small size. We show that the size and morphology of the supported nanoparticles together with strong Ni-support bonding and charge transfer at the step edge are key to the high catalytic activity towards methane activation, allowing much better activity than expected from earlier linear scaling relations [4-6]. The emphasis is here put on theoretical studies in combination with experiments using ambient pressure X-ray photoelectron spectroscopy, adsorption calorimetry and surface analysis measurements.

We thank Zhongtian Mao and Charles T. Campbell (UW) as well as the experimental group led by José A. Rodríguez and Sanjaya Senanayake (BNL) for their cooperative work. The collaboration of Agustín Salcedo and Beatriz Irigoyen (ITHES, CONICET-UBA, Argentina) is acknowledged.

- [1]. Z. Liu, D. C. Grinter, P. G. Lustemberg, T. Nguyen-Phan, Y. Zhou, S. Luo, I. Waluyo, E. J. Crumlin, D.J. Stacchiola, J. Zhou, J. Carrasco, H. F. Busnengo, M. V. Ganduglia-Pirovano, S. D. Senanayake, and J.A. Rodríguez, *Angew. Chem. Int. Ed.* **55** (2016) 7455-7459.
- [2]. P. G. Lustemberg, P. J. Ramírez, Z. Liu, R. A. Gutiérrez, D. G. Grinter, J. Carrasco, S. D. Senanayake, J. A. Rodríguez, and M. V. Ganduglia-Pirovano, *ACS Catal.* **6** (2016) 8184-8191.
- [3]. P. G. Lustemberg, R. M. Palomino, R. A. Gutiérrez, D. C. Grinter, M. Vorokhta, Z. Liu, P. J. Ramírez, V. Matolín, M. V. Ganduglia-Pirovano, S. D. Senanayake, and J. A. Rodríguez, *J. Am. Chem. Soc.* **140** (2018) 7681-7687.
- [4]. Z. Mao, P. G. Lustemberg, J. Rumpitz, M. V. Ganduglia-Pirovano, C. T. Campbell, *ACS Catal.* **10** (2020) 5101-5114.
- [5]. P. G. Lustemberg, F. Zhang, R. A. Gutiérrez, P. J. Ramírez, S. D. Senanayake, J. A. Rodríguez and M. V. Ganduglia-Pirovano, *J. Phys. Chem. Lett.* **11** (2020) 9131-9137.
- [6]. P. G. Lustemberg, Z. Mao, A. Salcedo, B. Irigoyen, M. V. Ganduglia-Pirovano, C. T. Campbell, *ACS Catal.* **11** (2021) 510604-10613.