

In situ X-ray absorption spectroscopy (XAS) study of CeO₂-based catalysts for CO₂ to methane conversion

Irene Barba-Nieto¹, Yuxi Wang¹, Jorge Moncada¹, Juan D. Jimenez¹, Marcos Fernández-García² and José Rodríguez^{1,3}

¹ *Chemistry Division, Brookhaven National Laboratory, Upton, New York 11973 (USA)*

² *Instituto de Catálisis y Petroleoquímica, CSIC.C/Marie Curie 2, 28049, Madrid (Spain)*

³ *Department of Chemistry, Stony Brook University, Stony Brook, New York 11794 (USA)*

Carbon dioxide (CO₂) is the primary gas responsible for the greenhouse effect in Earth's atmosphere, leading to higher global temperatures and climate change. In order to limit global warming to 1.5 °C and achieve net zero carbon dioxide emissions by 2050, it is essential to advance industrial processes that facilitate the generation of clean fuels from CO₂; one of the most promising strategies in this regard is the utilization of CO₂ and its transformation into valuable chemicals.

This study examines the effectiveness of two catalyst types, Ru-CeO₂ and Ru-CeO₂-TiO₂ systems, for the conversion of CO₂ into methane. The results demonstrate that, despite a lower Ru content, TiO₂-containing systems exhibit significantly enhanced catalytic activity for CO₂ conversion to methane. To understand this fact, in situ X-ray absorption measurements have been carried out on the Ru K-edge and Ce L₃-edge analyzing their behavior under H₂, CO₂ and H₂+CO₂.

The XAS findings indicate that the presence of TiO₂ in the catalysts stabilizes the metallic state of Ru, which remains in this state during the methanation reaction. Moreover, TiO₂ promotes the formation of Ce³⁺, enhancing the catalysts' reactivity. This effect is attributed to TiO₂ facilitating an electronic transfer at the interface and perturbing the regular fluorite geometry of ceria, thus promoting the presence of Ce³⁺. The presence of Ce³⁺ significantly impacts the catalytic properties of the sample, aiding in the oxidation-reduction of Ce and stabilizing Ru. Consequently, the presence of reduced cerium plays a crucial role in determining the surface chemistry of the catalyst, crucial for efficiently converting CO₂ into methane.

⁺ Author for correspondence: mbarbanie1@bnl.gov