

Design of selective, stable, and scalable ZnZrO_x catalysts for sustainable methanol synthesis from CO₂

T. Zou¹, T. Pinheiro Araújo¹, J. Morales-Vidal², M. Agrachev¹, P. O. Willi¹, R. N. Grass¹, G. Jeschke¹, S. Mitchell¹, N. López², J. Pérez-Ramírez^{1*}

¹ETH Zurich, ²Institute of Chemical Research of Catalonia

Mixed zinc-zirconium oxides (ZnZrO_x) are highly selective and stable catalysts for methanol production via catalytic carbon dioxide hydrogenation, a more sustainable route to produce this vital energy carrier and commodity. However, a lack of in-depth understanding of descriptors governing reactivity and stability of ZnZrO_x catalysts hinder the performance improvements required for effective industrial implementation. The coprecipitation (CP) method typically employed in preparing ZnZrO_x systems is also constrained by Zn incorporation into the bulk of ZrO₂, leading to catalysts with low surface area and suboptimal CO₂ adsorption capacity.^[1] Here, we conduct a systematic comparison of ZnZrO_x catalysts synthesized by flame spray pyrolysis (FSP, **Fig. 1a**) and wet impregnation (WI) to coprecipitated analogues, to establish detailed synthesis-structure-performance relationships. FSP and WI systems display up-to 3-fold higher methanol productivities than their CP counterparts (**Fig. 1b**) with stable performance in both pure CO₂ and hybrid CO-CO₂ feeds, by maximizing surface area as well as the formation of atomically dispersed Zn²⁺ sites incorporated in lattice positions within the ZrO₂ surface, as revealed by electron microscopy (**Fig. 1c**) and confirmed by operando X-ray absorption spectroscopy (XAS). In situ electron paramagnetic resonance (EPR) spectroscopy demonstrates that the catalyst architectures resulting from FSP and WI markedly foster the generation of oxygen vacancies (V_O).^[2] Kinetic and computational modelling show that these vacancies create active ensembles with surrounding Zn and Zr-O atoms (**Fig. 1c** inset) that favor methanol production through the formate pathway while suppressing CO formation.^[2] This work elucidates the nature of active sites, their correlation to experimental fingerprints and working mechanisms, and provides a scalable synthetic pathway and design guidelines for this cost-effective and earth-abundant catalyst family in sustainable methanol synthesis.

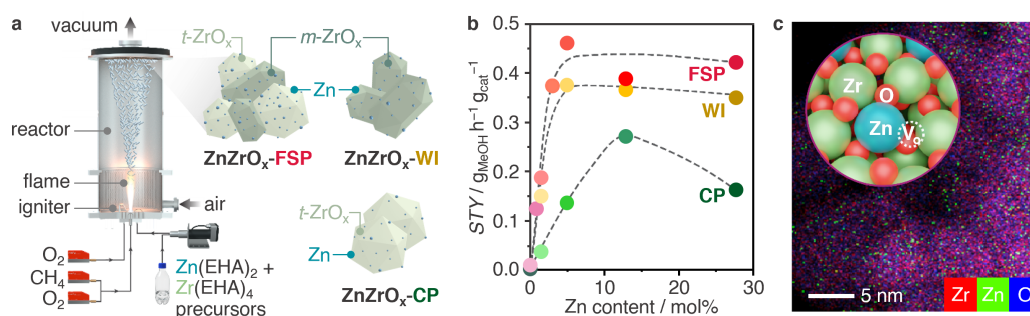


Fig. 1a Scheme of the FSP setup for ZnZrO_x catalysts and the resultant ZrO₂ polymorphs of FSP, WI, and CP catalysts. **b** Methanol space-time yield (STY) during CO₂ hydrogenation over ZnZrO_x catalysts prepared by different methods with varying Zn content, at 593 K, 5 MPa, H₂/CO₂ = 4, and GHSV = 24,000 cm³_{STP} h⁻¹ g_{cat}⁻¹. **c** Energy dispersive X-ray (EDX) maps of the used FSP-made ZnZrO_x catalyst with 5 mol% Zn, with a representative model of the most active m-ZnZrO_x catalytic ensemble shown in the inset.

[1] Zhe Han, Chizhou Tang, Feng Sha, Shan Tang, Jijie Wang, Can Li, *J. Catal.* **2021**, 396, 242-250.

[2] Thaylan P. Araújo, Jordi Morales-Vidal, Tangsheng Zou, Mikhail Agrachev, Simon Verstraeten, Patrik O. Willi, Robert N. Grass, Gunnar Jeschke, Sharon Mitchell, Núria López, Javier Pérez-Ramírez, *Adv. Energy Mater.* **2023**, 13, 2204122.