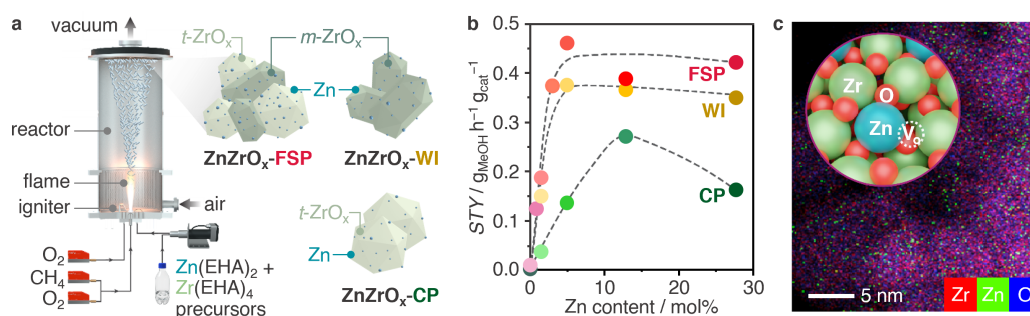


## Design of selective, stable, and scalable ZnZrO<sub>x</sub> catalysts for sustainable methanol synthesis from CO<sub>2</sub>

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Mixed zinc-zirconium oxides (ZnZrO<sub>x</sub>) 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<sub>x</sub> catalysts hinder the performance improvements required for effective industrial implementation. The coprecipitation (CP) method typically employed in preparing ZnZrO<sub>x</sub> systems is also constrained by Zn incorporation into the bulk of ZrO<sub>2</sub>, leading to catalysts with low surface area and suboptimal CO<sub>2</sub> adsorption capacity.<sup>[1]</sup> Here, we conduct a systematic comparison of ZnZrO<sub>x</sub> 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 CO<sub>2</sub> and hybrid CO-CO<sub>2</sub> feeds, by maximizing surface area as well as the formation of atomically dispersed Zn<sup>2+</sup> sites incorporated in lattice positions within the ZrO<sub>2</sub> 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<sub>O</sub>).<sup>[2]</sup> 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.<sup>[2]</sup> 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<sub>x</sub> catalysts and the resultant ZrO<sub>2</sub> polymorphs of FSP, WI, and CP catalysts. **b** Methanol space-time yield (STY) during CO<sub>2</sub> hydrogenation over ZnZrO<sub>x</sub> catalysts prepared by different methods with varying Zn content, at 593 K, 5 MPa, H<sub>2</sub>/CO<sub>2</sub> = 4, and GHSV = 24,000 cm<sup>3</sup><sub>STP</sub> h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. **c** Energy dispersive X-ray (EDX) maps of the used FSP-made ZnZrO<sub>x</sub> catalyst with 5 mol% Zn, with a representative model of the most active m-ZnZrO<sub>x</sub> 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.