Design of selective, stable, and scalable $ZnZrO_x$ catalysts for sustainable methanol synthesis from CO_2

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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 ZrO_2, leading to catalysts with low surface area and suboptimal CO_2 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 CO_2 and hybrid CO-CO_2 feeds, by maximizing surface area as well as the formation of atomically dispersed Zn^{2+} sites incorporated in lattice positions within the ZrO_2 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.

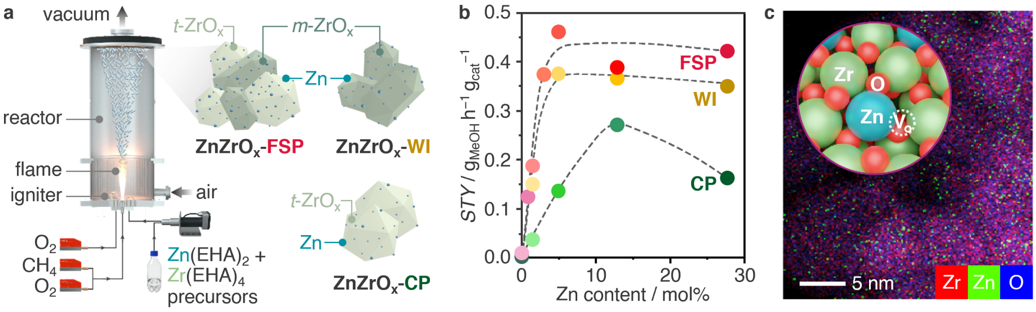

Fig. 1a Scheme of the FSP setup for $ZnZrO_x$ catalysts and the resultant ZrO_2 polymorphs of FSP, WI, and CP catalysts. **b** Methanol space-time yield (*STY*) during CO_2 hydrogenation over $ZnZrO_x$ catalysts prepared by different methods with varying Zn content, at 593 K, 5 MPa, $H_2/CO_2 = 4$, and $GHSV = 24{,}000\ cm^3_{STP}\ h^{-1}\ g_{cat}^{-1}$. **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.

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