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Zeolite Framework Induced Regioselectivity in Rh-Catalyzed Hydroformylation of α-Olefins

Fischer–Tropsch synthesis (FTS) converts syngas (H_2 + CO), readily obtained from coal or biomass gasification and natural-gas reforming, into ultra-clean fuels and chemicals. Linear α-olefins (LAOs) constitute a substantial fraction of the product distribution and represent high-value intermediates that are otherwise challenging to access. Conventional ethylene oligomerization typically affords only a limited set of even-carbon LAOs (*e.g.*, 1-hexene), whereas FTS uniquely delivers a broader spectrum that includes both even- and odd-carbon homologues. Isolation of these LAOs from complex FTS product mixtures remains difficult, however, because their physical properties closely resemble those of the co-produced alkanes of identical carbon number, severely limiting direct industrial utilization.

Catalytic hydroformylation provides an attractive dual-purpose strategy for upgrading FTS-derived LAOs. When the mixed (LAO + alkane) streams are subjected to hydroformylation, the alkanes remain unreactive while the olefins are selectively converted into aldehydes. The resulting substantial increase in boiling-point difference between the aldehydes and the residual alkanes greatly facilitates downstream separation. The aldehydes themselves are versatile precursors for plasticizers, solvents, coatings, and pharmaceuticals. Traditional homogeneous rhodium catalysts deliver high activity and selectivity for this transformation, yet they present formidable challenges in catalyst recovery and recycling. Heterogeneous alternatives circumvent separation issues but typically suffer from diminished regio- and chemo-selectivity because the metal centers lack precise steric and electronic control.

In this talk I will describe our recent efforts to overcome these limitations by encapsulating molecularly defined Rh centers within the confined microenvironment of zeolite frameworks.[1,2,3] The zeolite scaffold precisely orients reaction intermediates, enabling exceptional regio- and chemo-selectivity toward the desired linear aldehydes while retaining the robustness and recyclability of a solid catalyst. Mechanistic, spectroscopic, and computational studies reveal how the constrained interfacial coordination environment governs product distribution. Beyond the valorization of FTS-derived LAOs, this confined-catalysis strategy[4,5] offers a general platform for the rational design of selective heterogeneous catalysts that promote atom-economical and energy-efficient transformations of carbon-based resources.

References:

[1] Zhang, X., Yang, Y.*, Cao, Z.* et al. *Nature*, 2024, 629, 597–602.[2] Dou, X., Cao, Z.*, Liu, L.* et al. *Nat. Catal.*, 2024, 7, 666–677; [3] Yan, T., Cao, Z.* et al. *Natl. Sci. Rev.*, 2026, 13, nwag110; [4] Zhou, Z., Cao, Z.* et al. *Angew. Chem. Int. Ed.*, 2025, 64, e202419900; [5] Chang, H., Cao, Z.* et al. *Natl. Sci. Rev.*, 2026, 13, nwaf502.