Dynamic Confinement Approach for High Metal Loading Crystalline Single-Atom Catalysts

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Single-atom catalysts (SACs) bridge the gap between homogeneous and heterogeneous catalysis by combining molecular-level control and selectivity with structural robustness and scalability, achieved through atomically dispersed metal active sites [1]. However, their practical deployment is often limited by metal atom aggregation at elevated loadings, which compromises catalytic performance. Herein, we report a new synthetic strategy for the preparation of high-loading SACs based on palladium polyphthalocyanine covalent organic frameworks (COFs) using a mixed-metal ionothermal approach [2]. The method relies on the cyclization of tetracyanobenzene and tetracyanopyrazine in molten salt systems containing $PdCl_2/ZnCl_2$ or $PdCl_2/ZnCl_2/NaCl$, enabling simultaneous framework formation and palladium incorporation. The resulting crystalline materials exhibit atomically dispersed palladium species with metal loadings approaching 23 wt%. When evaluated under continuous flow conditions, these catalysts demonstrate stable activity, achieving yields of up to 90% and maintaining performance over 24 hours, establishing a new benchmark for metal loading and operational stability in SAC systems.

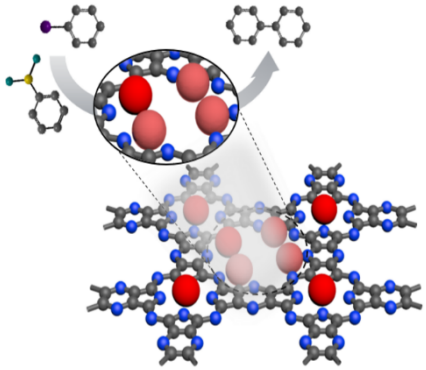

Figure 1. Dynamic confinement approach for ultra-high-loading Pd single atoms in phthalocyanine COFs

[1] Giannakakis, G.; Mitchell, S.; Pérez-Ramírez, J.,*Trends Chem.* **2022**, *4*, 264–276.
[2] Song, K. S.; Fritz, P. W.; Abbott, D. F.; Poon, L. N.; Caridade, C. M.; Gándara, F.; Mougel, V.; Coskun, A., *Angew. Chem. Int. Ed.* **2023**, *62*, e202309775.