Ruthenium Single-Atom Sites Stabilized on Functionalized Al-MOF for Electrochemical Hydrogenation

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The development of efficient catalysts for electrochemical hydrogenation (ECH) requires precise control over active site dispersion and substrate–catalyst interactions. Herein, we report a post-synthetic modification strategy to engineer Al-MOF-303 for stabilizing atomically dispersed ruthenium sites for ECH applications. The parent Al-MOF-303 was functionalized with aniline to introduce nitrogen-rich coordination environments, enabling the anchoring of isolated Ru atoms within the framework.

Structural integrity of the modified material was confirmed by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and solid-state 13^{13} 13 C NMR. Aberration-corrected HAADF-STEM and X-ray absorption spectroscopy (XAS) analyses verify the atomic dispersion of Ru and reveal a well-defined Ru–N_x coordination environment. X-ray photoelectron spectroscopy indicates a Ru oxidation state close to +3, suggesting strong metal–ligand interactions that stabilize the active sites.

Electrochemical hydrogenation studies demonstrate that the Ru single-atom catalyst exhibits enhanced activity and selectivity compared to the pristine and modified MOF counterparts. The improved performance is attributed to the synergistic interplay between isolated Ru sites and nitrogen coordination, which promotes efficient adsorption and activation of reactant molecules while modulating hydrogen adsorption behavior. Furthermore, the tailored coordination environment suppresses competing hydrogen evolution, enabling improved hydrogen utilization efficiency.

This work highlights that functionalization of MOFs provides a versatile platform for stabilizing single-atom catalysts and tuning their catalytic properties for electrochemical hydrogenation. The findings offer insights into the rational design of MOF-based single-atom electrocatalysts for selective hydrogenation reactions.

Keywords:
Single-atom catalyst, Metal–organic framework (MOF), Functionalization, Electrochemical hydrogenation, Ru–N coordination