

Precise Synthesis and CO₂ Hydrogenation Catalysis of Early-Transition Metal Clusters

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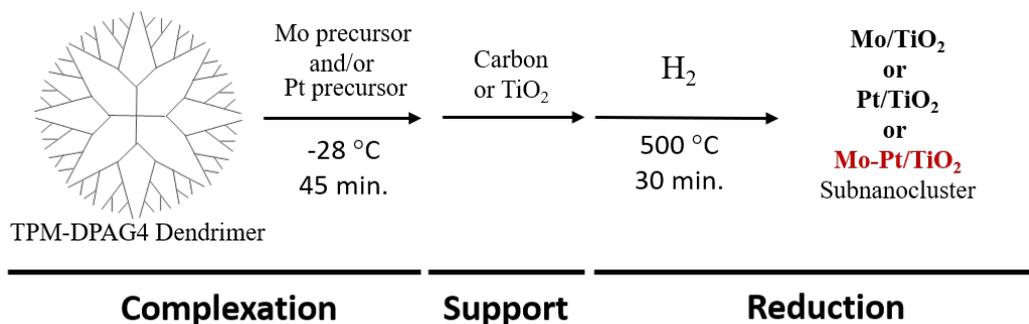
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Ultra-small subnanoclusters exhibit unique properties compared to their nanoparticles and metal bulks, such as high catalytic activity. In this context, ultra-small precious metal clusters like Platinum have been extensively investigated.¹⁻³ This research targeted early-transition metals such as Molybdenum. We have succeeded in precisely synthesizing Mo clusters on carbon and TiO₂ support using the carbothermal hydrogen reduction (CHR) method at 500 °C by employing a phenylazomethine dendrimer as a template. By utilizing the potential gradient within the dendrimer molecule, we have also succeeded in precisely synthesizing the Mo-Pt bimetallic subnanocluster supported on TiO₂.

The formation and characteristics of clusters were confirmed using X-ray photoelectron spectroscopy (XPS), high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray absorption fine structure (XAFS) studies. We found that Mo clusters with less than 1.3 nm formed oxycarbides, and Mo nanoparticles larger than 1.3 nm formed carbides on a carbon support. It indicates a size-dependent phase transformation, what we called subnano-transformation.⁴

We have evaluated the catalytic activity of Mo-based clusters, including Mo-Pt/TiO₂ bimetallic subnanocluster, on the CO₂ hydrogenation under mild temperature (T = 150 °C). It revealed that alloying and subnano-ization of Mo-Pt particles resulted in a high turnover number of CO₂ compared to Mo-only and Pt-only subnanoclusters and nanoparticles.



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