Partially Thiolated Au Cluster Catalysts on Layered Double Hydroxide: Atomic-Level Size Effect on Oxidation Catalysis

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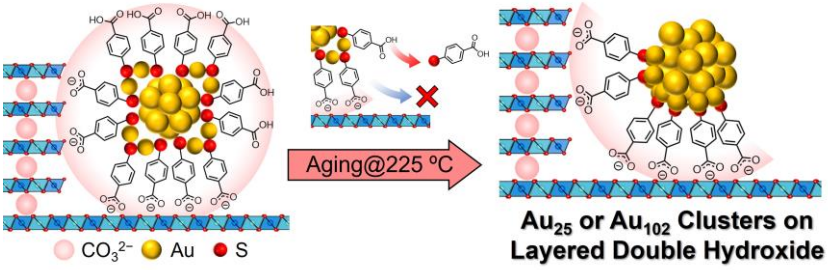
Gold nanoparticles smaller than ~2 nm exhibit size-specific oxidation catalysis.[1)] However, the size effects is still poorly understood at the atomic level and the scope of the catalytic applications remains limited for two reasons: difficulty in the atomically precise synthesis of active site and low durability of the Au clusters. The former issue has been overcome by removing the ligands from pre-synthesized ligated Au_n clusters immobilized on solid substrates.[2)] For the latter issue, we have recently found that residual ligands after controlled calcination stabilized the Au_n cluster on carbon supports by van der Waals interaction without affecting the catalytic activity.

In this work, we attempted to extend the scope of this approach by stabilizing partially ligated Au clusters on a support using electrostatic interactions. Specifically, we calcined *p*-mercaptobenzoic acid (*p*MBA)-protected Au_n clusters (n = 25 or 102) with anionic charge on a layered double hydroxide (LDH) with intercalated charge compensating anions between brookite-type lamellar structures. Au L_3-edge X-ray absorption fine structure analysis suggested that some of the *p*MBA ligands remained while retaining the original size of Au_n sites even after long-term aging at 225 °C under air (Scheme 1). Thanks to the residual *p*MBA ligands, Au_n-immobilized LDHs showed high stability during the oxidation of 5-hydroxymethylfurfural (HMF) at 80 °C. We revealed a significant size effect on a rate-determining step of the HMF oxidation for the first time. More details on the structures and the difference of reactivity will be given in the presentation.



Scheme 1. Atomically precise synthesis of Au_n active sites on LDH by electrostatic interactions

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