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Ligands Modulate Reaction Pathway in the Hydrogenation of 4-Nitrophenol Catalyzed by Gold Nanoclusters (Article)

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Abstract

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Protective ligands are key components of ligand-protected metal nanoclusters (NCs), as they offer good stability and multiple functionalities to the metal NCs in solution. Herein, we demonstrated that the ligand landscape on the NC surface could also be used to modulate the catalytic active sites of metal NCs in solution thus to direct the catalytic reaction towards desirable products through a different pathway. We found that thiolate ligands, namely, p-mercaptobenzoic acid (p-MBA), in $Au_{25}(p-MBA)_{18}$ NCs could influence the reaction pathway in the catalytic hydrogenation of 4-nitrophenol in solution. In particular, the well-defined ligand structure of $Au_{25}(p-MBA)_{18}$ NCs in solution provided a unique environment for the coadsorption of two substrate molecules (4-nitrophenol) on the Au NC surface, and this ligand modulation could activate a reaction pathway involving the formation of azobenzene intermediates from the two adsorbed substrate molecules, which are missing in nanogold catalysts without protective ligands. The discovery of this alternative reaction pathway highlights the importance of ligands on nanogold catalysts in modulating their active sites and directing their catalytic reaction pathways in solution and provides good opportunities to tailor the selectivity of ligand-protected metal NC catalysts. © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

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