Theoretical investigation of CO_2 electroreduction on atomically precise nickel nanoclusters

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Electrochemical CO_2 reduction reaction (CO_2RR) is a powerful strategy to control the increasing levels of CO_2 emission in atmosphere. Thiolate-protected nickel nanoclusters (NCs) have recently received a significant interest as a promising material for various electrocatalytic applications. Herein, we performed density functional theory calculations to explore CO_2 reduction and the competing hydrogen evolution reaction (HER) on $Ni_4(SCH_3)_8$ (Ni_4) and Au-doped $Au_4Ni_2(SCH_3)_8$ (Au_4Ni_2) NCs. It was determined that fully thiolate protected NCs exhibited low activity towards both reactions. We found that a portion of the thiolate ligands can be removed under the reducing potential and this significantly improved the catalytic activity of both NCs. After partial ligand removal, Ni_4 NCs were highly active towards HER, however, they were poisoned by CO* at CO_2 reduction conditions. Therefore, we investigated the energetics of CO_2RR and HER on CO*-adsorbed NCs. It was found that implanted Au sites of Au_4Ni_2 NCs do not get poisoned by *CO's, and they are critical in promoting the CO_2RR activity while suppressing the HER activity particularly under CO poisoning conditions.