447d Hydrogen Peroxide Formation and Propylene Epoxidation on Gas-Phase Au Clusters

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Abstract

We report a detailed DFT (B3LYP) analysis of the gas-phase H_2O_2 formation from H_2 and O_2 on the Au_3, and Au_4^+. We find that H_2, which interacts only weakly with the Au clusters, is dissociatively added in the Au-O bond, upon interaction with the Au_nO_2. Once formed, the hydroperoxy (OOH) intermediate acts as a precursor for the closed-loop catalytic cycle. The second H_2 addition to form H_2O_2 is the rate determining step (RDS) of the close loop catalytic cycle. The H_2O_2 desorption is followed by O_2 addition to Au_nH_2 to form the hydroperoxy intermediate, thus leading to the closure of the cycle. Based on the Gibb's free energy of activation, Au_4^+ is more active than Au_3 for the formation of the H_2O_2. In the next step, we also studied the propylene epoxidation on the neutral Au_3, with hydroperoxy intermediate as the precursor. The more electrophilic O atom (proximal to the Au) of the OOH group attacks the C=C of the propylene to form PO, with an activation barrier of 19.5 kcal/mole. Although the activation barrier of the RDS in this mechanism (with no Ti involved) is somewhat higher than that in the published olefin epoxidation mechanisms on the Ti site (with no Au involved), our pathway is a potential PO formation channel, with only Au playing a direct role in the reaction.