

DFT calculations for Aerobic Oxidation of Alcohols over Neutral Au₆ Cluster

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In recent years, gold supported catalyst has been attracting scientific and industrial interests owing to its catalytic activity for many reactions such as CO oxidation, odor decomposition, propylene epoxidation, and direct H₂O₂ production at low temperatures. Lately, Tsukuda has found that the Au nanoclusters stabilized by poly(N-Vinyl-2-pyrrolidone) [PVP; (C₆H₉ON)_n], abbreviated to Au:PVP, can oxidize *p*-hydroxybenzyl alcohol selectively into the corresponding aldehyde in water without degradation. This observation indicates that Au cluster can exhibit high catalytic activity without any metal oxide supports. From our previous work, it was found that the existence of the PVP plays an important role for the evolution of the active Au clusters. However, the catalytic activity of neutral Au clusters is not investigated in detail. In order to examine the catalytic activity of neutral Au clusters, the aerobic oxidation of *p*-hydroxybenzyl alcohol to the corresponding aldehyde catalyzed by Au₆ has been investigated quantum chemically using density functional theory with the PBE0 functional. Possible reaction pathways are investigated taking account of full structure relaxation of the model systems.

From the calculation results, it was found that the formations of both a hydroperoxyl anion and a hydride were the important steps for the aerobic oxidation of *p*-hydroxybenzyl alcohol over Au₆ cluster.

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