

Elucidation of active site and reaction mechanism of Pd/Au/CeO₂-catalyzed α,β -dehydrogenation of ketones

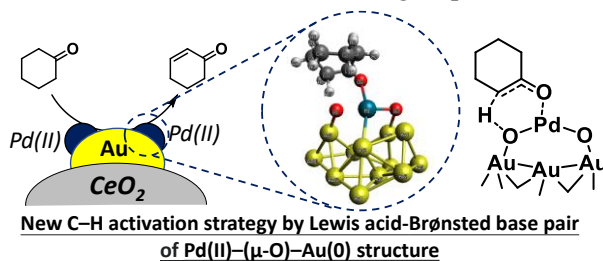
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Aerobic α,β -dehydrogenation of ketones to α,β -unsaturated ketones, which are present in bioactive substances and versatile organic synthetic intermediates, is an attractive transformation. Recently, we have reported heterogeneously catalyzed aerobic α,β -dehydrogenation of ketones including cyclohexanones via α -C–H activation for the first time using a Pd–Au bimetallic nanoparticle catalyst supported on CeO₂ (Pd/Au/CeO₂).¹ This catalytic system was truly heterogeneous, but it showed much higher catalytic activity for α,β -dehydrogenation of cyclohexanone than previously reported homogeneous catalysts.²

In this study, we experimentally and computationally elucidated the active site and mechanism of Pd/Au/CeO₂-catalyzed α,β -dehydrogenation of cyclohexanone via efficient C–H bond activation.³ Detailed characterization of the catalyst revealed that bimetallic nanoparticles are formed on the CeO₂ support with an average size of about 2.5 nm and comprising an Au nanoparticle core and PdO nanospecies dispersed on the core. Activity tests and detailed characterizations demonstrated that the dehydrogenation activity increased with the coordination numbers of Pd–O species in the presence of Au(0) species. Such experimental evidence suggests that a Pd(II)–(μ -O)–Au(0) structure is the true active site for this reaction. Density functional theory (DFT) calculations using a suitable Pd₁O₂Au₁₂ cluster model with the Pd(II)–(μ -O)–Au(0) structure proposed a C–H bond activation mechanism via concerted catalysis in which the Pd atom acts as a Lewis acid and the adjacent μ -oxo species acts as a Brønsted base simultaneously. The calculated results reproduced various experimental results for the selective formation of 2-cyclohexen-1-one from cyclohexanone without forming phenol, the regioselectivity of the reaction, the turnover-limiting step, and the activation energy.



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