

Aerobic Dehydrogenation of Saturated Ketones Using CeO₂-Supported Pd-on-Au Bimetallic Nanoparticle Catalysts

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α,β -Unsaturated carbonyl compounds are important in organic synthesis because they are useful as not only bioactive substances but also synthetic intermediates. One of the ideal α,β -unsaturated ketone syntheses is direct α,β -dehydrogenation of saturated carbonyl compounds. The α,β -dehydrogenation was typically performed using a stoichiometric amount of oxidants with the corresponding byproducts. Recently, environmentally-friendly aerobic α,β -dehydrogenations have been developed using homogeneous Pd(II) catalysts.^{1,2} However, to our knowledge, there are no reports on selective α,β -dehydrogenation using O₂ in the presence of supported Pd heterogeneous catalysts, although heterogeneously catalyzed systems have many advantages in terms of green chemistry.

In this study, we successfully prepared a dispersed Pd(II)-on-Au bimetallic nanoparticle catalyst supported on CeO₂ (Pd/Au molar ratio = 1/5, Pd/Au/CeO₂), which enabled heterogeneously catalyzed aerobic selective α,β -dehydrogenation of saturated ketones to α,β -unsaturated ketones for the first time.³ We carried out the dehydrogenation of cyclohexanone, a typical saturated ketone, using supported nanoparticle catalysts (Table 1). While CeO₂-supported Au nanoparticles (Au/CeO₂, entry 2), CeO₂-supported Pd nanoparticles (Pd/CeO₂, entry 3) or physical mixture of Au/CeO₂ and Pd/CeO₂ (entry 4) did not catalyze the aerobic dehydrogenation, Pd/Au/CeO₂ specifically showed a high catalytic activity (TOF = 122 h⁻¹ based on Pd) for the α,β -dehydrogenation compared with those of previously reported homogeneous systems (2–3 h⁻¹).^{1,2} Besides cyclohexenones, this system has a wide range of substrate scopes; various α,β -unsaturated compounds, including bioactive substances and enaminones, can be synthesized from the corresponding saturated ketones (22 examples).

1) M. Tokunaga, S. Harada, T. Iwasawa, Y. Obora, Y. Tsuji, *Tetrahedron Lett.*

2007, *48*, 6860. 2) T. Diao, S. S. Stahl, *J. Am. Chem. Soc.* **2011**, *133*, 14566. 3) D. Takei, T. Yatabe, X. Jin, T. Yabe, N. Mizuno, K. Yamaguchi, *ACS Catal.* **2020**, *10*, 5057.

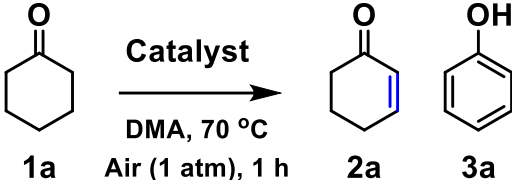
			
Entry	Catalyst (mol%)	Yield (%)	
		2a	3a
1	Pd/Au/CeO₂ (Pd: 0.6, Au: 3.0)	74	<1
2	Au/CeO ₂ (3.9)	<1	<1
3	Pd/CeO ₂ (4.9)	<1	<1
4	Pd/CeO ₂ (2.5) + Au/CeO ₂ (2.0)	<1	<1

Table 1. The effect of catalysts