Development of Selective Hydrogenation Pd black Catalyst Deposited on Pd Sheet

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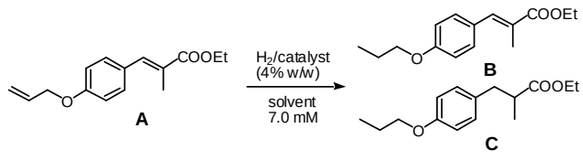
An effective method for high selective hydrogenation using palladium catalyst has been seldom reported in the literature. Selective hydrogenation of alkenes bearing different substitution olefins is quite difficult owing to concomitant hydrogenation reaction on each olefin. Recently, electrolysis-coupled hydrogenation system has been developed and achieved hydrogenolysis-free hydrogenation on various alkenes bearing benzylic ethers and esters. The essential point of selective hydrogenation reaction depends on the surface nature of Pd catalyst[1]. We have found a certain Pd black catalysts to be effective for selective hydrogenation. Reactivity and selectivity of Pd black catalysts depend on the method for deposition. On comparison with Pd catalysts that are easily available, the Pd black-(E) catalysts deposited on Pd sheet exhibited selective hydrogenation, remarkably (Table 1). "Pd black-(E)" means Pd black deposited on Pd sheet by galvanizing in 28 mM $PdCl_2$ / 1M HClaq. "Pd black-(H)" means Pd black deposited on Pd sheet by hydrogen reduction using occluded hydrogen in Pd sheet without an energy. In the case that Pd black–(E) was employed as a catalyst, the alkene having two different types olefin **1** was hydrogenated for 4h in toluene to give selective hydrogenation product **2** in quantitative yield. After 24 hours, the product **2** was still stable without being converted into the completely saturated compound **3**, and no by-products were obtained. The hydrogenation reaction was carried out by using commercially available Pd black[2], Pd-C and hand made Pd black, however, the **3** was formed immediately so that the **2** was not obtained selectively.

An aromatic hydrocarbon solvent (benzene, toluene) gave excellent result and other solvents such as petroleum ether, 1,4-dioxane, ethyl acetate and dichloromethane are also effective for selective hydrogenation reaction.

The other sheet deposited type catalyst Pd black-(H) has similar selectivity. Its detail will be report in the presentation. In addition, these deposited Pd catalysts keep their selective activity more than 1000 hours (Scheme 1).

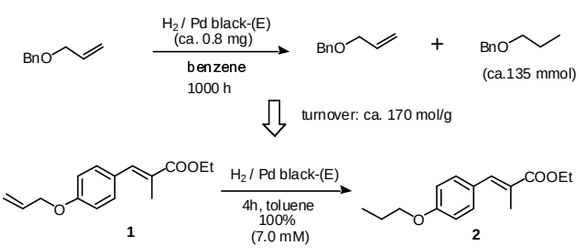
Table 1.



Catalyst (4% w/w)	Solvent	time (h)	**1** (%)	**2** (%)	**3** (%)
Pd black-(E)	toluene	1	9	91	0
		4	0	100	0
		24	0	100	0
	MeOH	1	0	0	100
Pd black (WAKO)	toluene	1	0	3	97
		4	0	0	100
	MeOH	1	0	0	100
5% Pd-C (Kawaken Chemical)	toluene	1	0	5	95
		4	0	0	100
	MeOH	1	0	0	100
Pd black* (handmade)	toluene	4	0	0	86
	MeOH	1	0	0	95
Pd sheet	toluene	48	100	0	0
	MeOH	48	100	0	0

* Pd-black produced by reducing $PdCl_2$ with HCOOH.

Scheme 1



References

1) S. Maki, Y. Harada, R. Matsui, M. Okawa, T. Hirano, H. Niwa, M. Koizumi, Y. Nishiki, H. Inoue and C. Iwakura, *Tetrahedron Letters*, **2001**, *42*, 8323-8327.

3) S. Maki, M. Okawa, R. Matsui, T. Hirano and H. Niwa,

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