

Development of Lead-free Semihydrogenation Catalyst Employing Core-Shell Structured Pd Nanoparticles

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Semihydrogenation of alkynes is a powerful method to synthesize (Z)-alkenes which are important intermediates for pharmaceuticals and natural products. However, the traditional semihydrogenation catalyst (Lindlar catalyst: Pd/CaCO₃-Pb(OAc)₂) has serious drawbacks such as the use of a toxic Pb salt, the addition of a large amount of quinoline to the reaction mixture and the limited substrate scope for internal alkynes.

Recently, we reported a practical and an efficient catalyst system for the semihydrogenation using silica-supported Pd nanoparticles (NPs) and a small amount of dimethyl sulfoxide (DMSO).^[1] In this system, DMSO coordinates to Pd NPs more strongly than product alkenes and inhibits the undesirable overhydrogenation of them. Herein, we developed the core-shell structured nanocomposite involving Pd NPs encapsulated by the solid matrix shell consisting of methylpropylsulfoxide species (Pd@MPSO/SiO₂).^[2] In this catalyst, the shell having MPSO network coordinates to the Pd NPs as a macroligand, promoting the selective semihydrogenation of alkynes. Pd@MPSO/SiO₂ showed excellent selectivity for the semihydrogenation of not only internal alkynes but also terminal ones without any additives. Furthermore, the catalyst was reusable without any loss of its activity or selectivity.

TEM images of Pd@MPSO/SiO₂ showed the formation of Pd NPs having core-shell structure (Figure 1). Further characterizations such as EDS, CO adsorption, and ¹³C CP/MAS-NMR analysis revealed that the shell was composed of MPSO matrix and the sulfur atom of MPSO was coordinated to Pd NP.

As shown in Figure 2a, semihydrogenation of 1-phenyl-1-propyne (**1**) proceeded in the presence of Pd@MPSO/SiO₂ under 1 atm of H₂ and (Z)-1-phenyl-1-propene (**2**) was obtained in 97% yield. Interestingly, the overhydrogenation of **2** to propylbenzene (**3**) didn't occur after complete conversion of **1**, while **2** was rapidly hydrogenated to **3** using Pd/SiO₂ as a catalyst. These results clearly showed that the MPSO shell of Pd@MPSO/SiO₂ suppressed the overhydrogenation of the alkene product. Pd@MPSO/SiO₂ could give various internal and

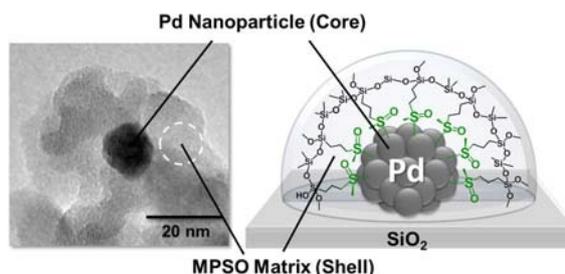


Figure 1. TEM and schematic image of Pd@MPSO/SiO₂.

terminal alkenes including valuable compounds as a fragrance from the parent alkynes (Figure 2b). After the reaction, the catalyst was easily recovered from the reaction mixture by centrifugation and could be reused with keeping its high alkene selectivity (Figure 2c).

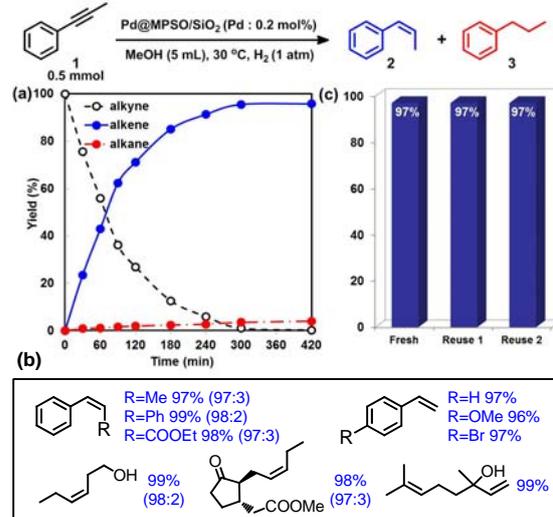


Figure 2. (a) Time course and for the hydrogenation of 1-phenyl-1-propyne catalyzed by Pd@MPSO/SiO₂. (b) Substrate scope and (c) results of reuse experiment of Pd@MPSO/SiO₂.

References

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