Silicon Nanostructure-Palladium Nanoparticle Hybrid Catalyst for Organic Transformation

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Abstract: We report the development of a silicon nanowire array-stabilized palladium nanoparticle catalyst, SiNA-Pd. It was applied to Mizoroki-Heck reaction, the hydrogenation of stilbene and nitrobenzene, the hydrosilylation of an enone, and the C-H arylation of thiophenes and indoles to provide a quantitative production with high reusability. In the hydrogenation, SiNA-Pd was reused more than 150 times without loss of catalytic activity. SiNA-Pd completed Mizoroki-Heck reaction within several hundred-mol ppb of palladium, reaching a TON of 2,000,000.

Keywords: Silicon nanowire array, Palladium nanoparticle catalyst, Cross-couplings

1. Introduction

Development of highly active and reusable solid catalysts is one of the most important topics not only for organic syntheses but also for chemical and pharmaceutical processes. Innovative nanodevices for catalytic transformations are expected to realize instantaneous, selective catalytic reaction systems. We envisioned that the development of hybrid catalysts of Pd nanoparticles and a silicon nanowire array as a macroscopic and nanoscopic hybrid catalyst would be promising for this purpose (Figure 1). Copious nanospaces can be provided on the surface of silicon wafer whose area is square centimeters wide. The hybrid catalysts should be equipped with confined nano-size reaction fields surrounded a lot of Pd nanoparticles (which should entropically drive the organic transformation in the nanospaces) with square centimeter wide of the silicon wafer (which should afford plenty of reaction capacity).

Here, we report a new platform for the catalytic reactions, a silicon nanowire array-stabilized palladium nanoparticle catalyst, SiNA-Pd. Its use in the palladium-catalyzed Mizoroki-Heck reaction, where the quantitative production of coupling compounds was achieved with 490 mol ppb (0.000049 mol %) Pd, is also presented. Moreover, SiNA-Pd promoted the hydrogenation of stilbene and nitrobenzene, the hydrosilylation of an enone, and the C-H arylation of thiophenes and indoles.[1] In the hydrogenation, SiNA-Pd was reused more than 150 times without loss of catalytic activity.

2. Experimental

The silicon nanowire array-stabilized Pd nanoparticle catalyst was prepared as follows (Figure 1): A *p*-type silicon wafer was treated with H_2SO_4/H_2O_2, and HF for wash and installation of Si-H, respectively. $AgNO_3$ reacted with the Si-H wafer to give an Ag nanoparticle-coated wafer that was treated with HF/H_2O_2, yielding the Ag nanoparticle-deposited silicon nanowire array. Removal of Ag nanoparticles and regeneration of Si-H surface were carried out with HNO_3 and HF, respectively. Immobilization of Pd

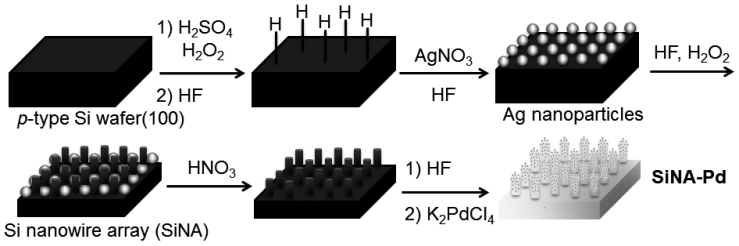
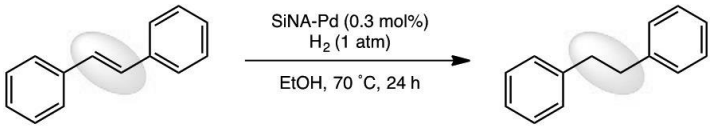


Figure 1. Preparation of SiNA-Stabilized Pd Nanoparticle Catalyst (SiNA-Pd).

nanoparticles was performed with K_2PdCl_4 on the silicon nanowire array to obtain the silicon nanowire array-stabilized Pd nanoparticle catalyst (SiNA-Pd).

3. Results and discussion

We applied SiNA-Pd to a variety of organic transformations. The hydrogenation of stilbene proceeded in the presence of SiNA-Pd (0.3 mol % Pd) in EtOH under hydrogen (1 atm) to give 1,2-diphenylethane with 99% yield. The catalyst was readily recovered and reused to afford 1,2-diphenylethane in 99% (100th use) and 99% (150th use) yield (Figure 2). SiNA-Pd was also applied to the C-H arylation of thiophenes (Figure 3). Thus, the reaction of iodobenzene with 2-methylthiophene was carried out with SiNA-Pd (0.3 mol %) and CsOAc in DMF to give 2-methyl-5-phenylthiophene with 80% yield (Figure 3). To attain the highest catalytic activity for the heterogeneous catalyst-promoted Mizoroki-Heck reaction, SiNA-Pd with 490 mol ppb Pd (0.000049 mol % Pd) was used for the reaction of the 10-gram scale substrate (Figure 4). When the reaction of iodobenzene (10.2 g) and butyl acrylate was performed with 490 mol ppb Pd of SiNA-Pd, butyl cinnamate was obtained with 95% yield. The turnover number (TON) and turnover frequency (TOF) were 2,000,000 and 40,000 h^{-1}, respectively. As far as we know, this is the highest TON for the Mizoroki-Heck reaction with heterogeneous catalysts. Ozagrel, an important antiasthmatic agent (thromboxane A2 synthesis inhibitor), was synthesized via the 490 mol ppb Pd SiNA-Pd-catalyzed Mizoroki-Heck reaction (Figure 4).



1st use 99%, **50th use** 99%, **100th use** 99%, **150th use** 99%

Figure 2. Reusability of SiNA-Pd in the Hydrogenation of stilbene

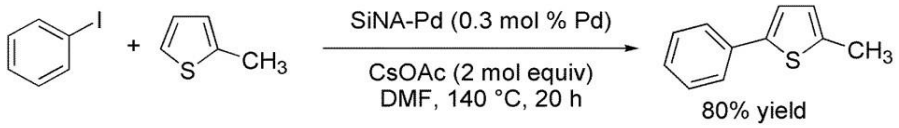


Figure 3. C-H Arylation of 2-Methylthiophene

4. Conclusions

We developed a highly active and reusable novel catalytic platform SiNA-Pd, a silicon nanowire array-stabilized palladium nanoparticle catalyst. We will show the detail of preparation of SiNA-Pd and its application to a variety of organic transformations in our poster presentation.

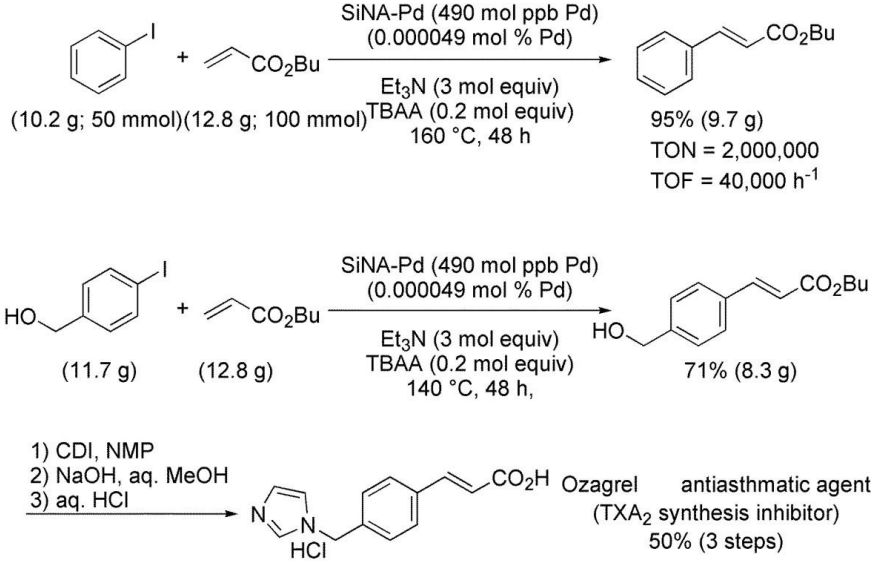


Figure 4. Mizoroki-Heck Reaction with 490 mol ppb (0.000049 mol %) Pd of SiNA-Pd, and the Synthesis of Ozagrel, an Antiasthmatic Agent

References

1. Y. M. A. Yamada,* Y. Yuyama, T. Sato, S. Fujikawa, Y. Uozumi, *Angew. Chem. Int. Ed.* **53**, 127-131 (2014)