Amorphous Alloy Pd-Ni-P Nanoparticle Catalyst for Selective Hydrogenation of Nitroarenes to Anilines

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Reduction of nitroarenes to access to poly-substituted anilines is one of the critical issues in chemical transformations because the functionalized anilines are key intermediates for the fine chemical, agrochemical, and pharmaceutical industries. Heterogeneous catalytic systems with molecular hydrogen as a reducing agent is favored in industry due to the recyclability of the catalyst, low-cost of hydrogen gas, and atom economic efficiency of the process. However, the selective reduction of the nitro group over other reducible groups in the same molecule is challenging. Although many catalytic systems have been developed for improving the selectivity, they have still some drawbacks not only on the chemoselectivity but also on the chemical yields, generation of by-products, large loading amounts of catalysts, difficulty of reuse of catalysts, requirement of additives, and harsh reaction conditions.

We envisaged that catalytic property of palladium can be controlled by formation of amorphous alloys. Here, we report the Pd-Ni-P amorphous alloy nanoparticles are quite effective catalysts for chemoselective reduction of nitroarenes, and the corresponding aniline derivatives are produced in high yields in the presence of 0.05 mol% of the catalyst under mild conditions without any additives. Various substrates with easily reducible substituents such as carbonyl, bromo, iodo, and nitrile groups proceed smoothly to give the corresponding anilines in high selectivity. The catalytic uniqueness of the amorphous catalyst was also confirmed by comparison with their crystalline counterpart. As expected, the latter afforded a lower selectivity. Moreover, the catalyst can be reused for 5 cycles without any catalytic activity loss. The reaction did not proceed after the catalyst was filtrated out. These results indicated the heterogeneity of the catalytic reaction.

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