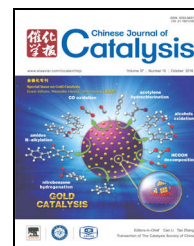


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Communication (Special Issue on Gold Catalysis)

Lewis acid-driven reaction pathways in synergistic cooperative catalysis over gold/palladium bimetallic nanoparticles for hydrogen autotransfer reaction between amide and alcohol

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ABSTRACT

Metal nanoparticle catalysts, especially gold and its bimetallic nanoparticle catalysts, have been widely used in organic transformations as powerful and green catalysts. The concept of employing two distinct catalysts in one reaction system, such as in cooperative and synergistic catalysis, is a powerful strategy in homogeneous catalysis. However, the adaption of such a strategy to metal nanoparticle catalysis is still under development. Recently, we have found that cooperative catalytic systems of gold/palladium bimetallic nanoparticles and Lewis acid can be used for the *N*-alkylation of primary amides through hydrogen autotransfer reaction between amide and alcohol. Herein, the results of a detailed investigation into the effects of Lewis acids on this hydrogen autotransfer reaction are reported. It was found that the choice of Lewis acid affected not only the reaction pathway leading to the desired product, but also other reaction pathways that produced several intermediates and by-products. Weak Lewis acids, such as alkaline-earth metal triflates, were found to be optimal for the desired *N*-alkylation of amides.

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Metal nanoparticles have recently attracted much attention as catalysts for organic synthesis because of their unique activities and selectivities, which are derived from both the characteristic nature of their surfaces and their electronic structures [1–11]. Among them, gold and its bimetallic nanoparticles have been found to be excellent catalysts for a range of redox processes such as aerobic oxidation, hydrogenation, and hydrogen transfer reactions [1–4,7,12–19].

We have developed a general strategy to encapsulate various kinds of single and bimetallic nanoparticles in polystyrene-based polymers with cross-linking moieties by using a strategy termed polymer incarceration (PI) [17,18,20]. Using

this methodology, we have prepared both single metal and bimetallic nanoparticle catalysts [20–26] and applied these unique catalytic systems to various organic transformations including redox reactions [20,23,24,26–32], cooperative catalysis [27,33,34], multistep tandem processes [30,35,36], and asymmetric transformations (Fig. 1) [37–39]. In these heterogeneous catalysts, metal nanoparticles are stabilized by multiple and weak interactions between the π -electrons of benzene rings and the surface of the metal nanoparticles. This characteristic interaction results in high activity and increased robustness of the catalysts, and suppresses leaching of metal nanoparticles and their aggregation.

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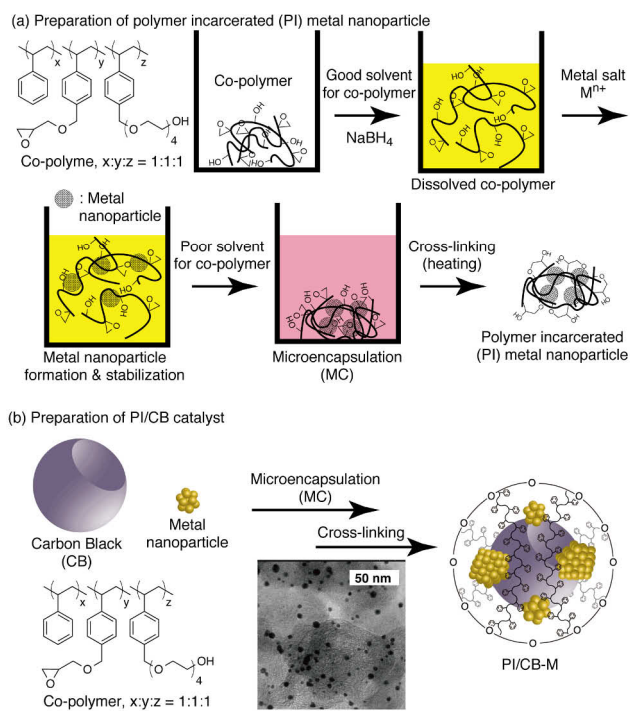
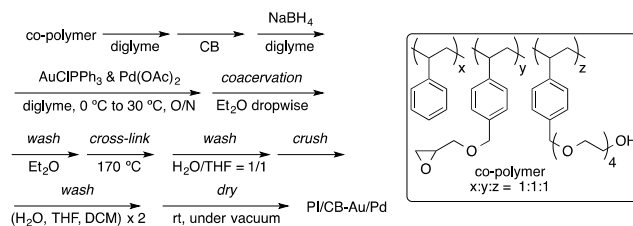


Fig. 1. Schematic image of the PI technique.

Hydrogen transfer/borrowing strategies are useful for conducting both C–C and C–heteroatom bond-formation reactions with high atom efficiency because these transformations are redox-neutral overall and no externally added oxidant or reductant is required [40–45]. In addition to the various homogeneous catalysts that have been developed for hydrogen transfer/borrowing reactions, metal nanoparticles have also been demonstrated to be effective catalysts for these transformations [46,47]. The alkylation of amines by using alcohols through hydrogen transfer/borrowing has been widely developed; however, examples of the *N*-alkylation of primary amides are quite limited [48–53]. This could be because amides are generally much less reactive than amines, so nucleophilic attack of a primary amide on an aldehyde generated *in situ* during the hydrogen transfer/borrowing process is difficult.

The strategy of utilizing two or more catalysts in one reaction system, so called synergistic or cooperative catalysis, is a very powerful tool for catalysis because it can lead to a dramatic reduction in the transition-state energy compared with those for single catalysts [54–56]. There are a number of synergistic or cooperative catalysts that involve metal complexes or organocatalysts; however, systems that are comprised of heterogeneous metal nanoparticles are still developing fields [27,33,34].

Recently, we developed synergistic cascade catalysts composed of a metal Lewis acid and gold/palladium (Au/Pd) bimetallic nanoparticles (Scheme 1; Fig. 2) for the *N*-alkylation of a primary amide with a primary alcohol through a hydrogen autotransfer mechanism. In this catalytic system, the choice of Lewis acids is crucial for smooth catalytic turnover and selection of reaction pathways [57]. After extensive optimization of reaction conditions, we have found that using 3 equivalents of



Scheme 1. Preparation of the PI/CB-Au/Pd catalyst.

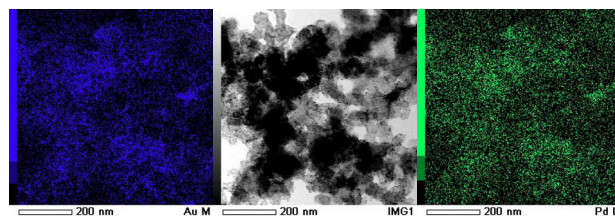
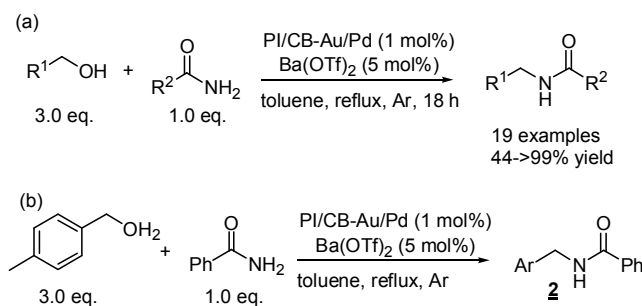


Fig. 2. STEM and EDS images of the PI/CB-Au/Pd catalyst.

alcohol in the presence of 1 mol% of PI/CB-Au/Pd and 5 mol% of Ba(OTf)₂ gave moderate to excellent yields of desired products with wide substrate scope (Scheme 2(a)). In addition, PI/CB-Au/Pd catalyst can be recovered and reused keeping high activity with simple operation (Scheme 2(b)). Several control experiments suggested that Lewis acids facilitate nucleophilic attack of a primary amide, which has much lower nucleophilicity than the corresponding amine, and this is the key to the success of this relatively challenging hydrogen autotransfer reaction. In the proposed reaction pathways, multiple reaction steps are elaborated and, in addition to the desired product, various intermediates and side-products are also formed (Fig. 3). In this communication, we describe the effect of Lewis acid on the complex reaction schemes in detail and discuss the correlation between the nature of the Lewis acid and the reaction pathway followed.

In a typical experiment, a Carousel® tube was charged with benzamide (30.3 mg, 0.25 mmol), PI/CB-Au/Pd (11.1 mg, 0.0025 mmol of Au) and a stirring bar. The carousel tube was then placed in an argon-filled glovebox. In the glovebox, additives, if any, were added (e.g. Ca(OTf)₂ (4.2 mg, 0.0125 mmol))



Run	1	2	3	4–11 ^a
Yield (%)	>99	99	53	95–99

^a Recovered catalyst was heated at 170 °C for 5 h under air before run 4, 7, and 10.

Scheme 2. Optimized reaction conditions for substrate scope and recovery & reuse of catalyst for *N*-alkylation of primary amide [57].

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