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Heck reaction catalyzed by flower-like cobalt nanostructures

Hongling Qi, Wu Zhang *, Xiang Wang, Hong Li, Jie Chen, Kaishan Peng, Mingwang Shao *

Anhui Key Laboratory of Functional Molecular Solids, College of Chemistry and Materials Science, Anhui Normal University, No. 1 Beijing East Road, Wuhu 241000, PR China

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ABSTRACT

Heck reaction catalyzed by flower-like cobalt nanostructures has been developed; the coupling of alkenes with aryl halides under ligand-free condition without the need to exclude air or moisture provides the corresponding products with moderate to good yields. More importantly, the cheap catalysts are stable under the reaction conditions and can be reused for at least six successive runs without any additional activation treatment.

1. Introduction

Heck reaction of aryl halide with olefins has recently been one of the most intensively studied transition-metal catalyzed carbon–carbon bond forming reactions and has been applied to many areas, including natural products [1,2] and fine chemicals [3]. Soluble palladiums, generally phosphine palladium complexes, are the most efficient catalysts for the Heck reaction. However, phosphine ligands are expensive, toxic, unrecoverable and sensitive to oxygen and water. What's worse, a homogeneous system has a major drawback related to product/catalyst separation. Further more, the catalyst recycling is often hampered by early precipitation of palladium and recovery of the expensive palladium is difficult. The problems could, in principle, be minimized using heterogeneous catalysts.

The application of transition-metal nanoparticles has attracted much attention during last ten years, especially for catalyzing the formation of carbon–carbon bond in heterogeneous system [4–8]. It was reported that palladium nanostructures such as hollow spheres or nanoparticles of different origins had been utilized in the Suzuki and Heck reaction [9–12]. Moreover, Heck-type reactions can be catalyzed by some other cheaper metals, such as Ni, Co, Cu, Fe and Ir or their complexes [13–16]. Though none of them can rival palladium in synthetic versatility, some features may complement Heck chemistry to provide either cheaper catalysts or catalysts capable of effective processing of some specific substrates. Therefore, it is of great interest to study the cheaper heterogeneous catalysts such as cobalt for Heck reaction.

The preparation, structure determination, and applications of cobalt nanostructures have been extensively studied due to their various properties and applications [17]. Recently, numerous efforts have been donated to develop new strategies for preparation of one-dimensional cobalt nanocrystals [18–20] and two-dimensional cobalt nanocrystals [21–23]. However, only limited three-dimensional cobalt nanostructures have been reported [24]. Furthermore, most of these reported nanostructures were achieved with the assistance of surfactants or polymers [25]. The post-treatment of these organic molecules usually destabilized the assembly architectures and resulted in difficulties for their potential applications as catalysts. So it is still challenging to the preparation of cobalt assembly nanostructures in absence of any surfactants.

In our current work, a facial approach for preparation of flower-like cobalt nanostructures in aqueous medium without any surfactants under sonication was established. More importantly, the obtained cobalt nanostructures exhibit superior catalytic activity in heterogeneous Heck reaction (Scheme 1) without protection of inert atmosphere. Moreover, it can be reused for at least six successive runs without any additional activation treatment.

2. Experimental

2.1. Preparation of cobalt nanostructures

All reagents involved in the experiments were commercially available and used without further purification. The typical preparation process was presented as follows: 0.0952 g $CoCl_2·6H_2O$ (0.4 mmol) and 0.012 g $NaBH_4$ (0.3 mmol) were dissolved in 10 mL de-ionized water respectively to form aqueous solution. Then $CoCl_2$ solution was injected slowly into $NaBH_4$ drop by drop

* Corresponding authors. Tel./fax: +86 553 3869310.
E-mail address: zhangwu@mail.ahnu.edu.cn (W. Zhang).

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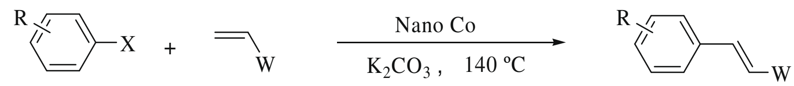

R = -H, $-OCH_3$, -Cl, $-NO_2$, -OH, -COOH, $-CH_3$. X = I, Br, Cl.

W = $-CO_2Me$, $-CO_2Et$, $-CO_2{}^{n}Bu$, -Ph.

Scheme 1. C–C coupling reaction.

under sonication at 30–40 °C. After the injection, the mixture was sonicated continuously for 10 min. Finally, the mixture was separated by centrifugation. The black precipitate was collected and washed with de-ionized water for several times, then dried in a vacuum oven at 60 °C for 4 h.

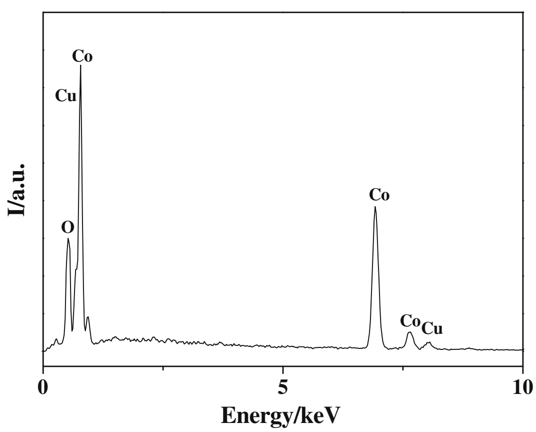

Fig. 1. EDS analysis of cobalt nanostructures.

2.2. Catalysis properties

In a typical experiment procedure for the Heck reaction: aryl halide (1 mmol), alkene (1.2 mmol), as-prepared cobalt products (0.02 mmol), K_2CO_3 (1 mmol) were placed in a two-neck round bottom flask with 2 mL of *N*-methylpyrrolidone (NMP). The reaction was carried out by submerging the round bottom flask in an oil bath preheated to 140 °C under reflux conditions for an appropriate time (monitored by TLC). After the reaction was completed, the round bottom flask was cooled down to room temperature and then centrifuged. The solution was separated and the precipitate was washed sufficiently with ether. The solutions were combined, washed with water for three times and purified by column chromatography on silica gel with appropriate eluent to yield the product. The precipitate was further washed sufficiently with water and ethanol then dried in a vacuum oven at 60 °C for 4 h, and the cobalt catalysts were recovered.

2.3. Characterization

The synthesized products were characterized by X-ray powder diffraction (Shimadzu XRD-6000) with graphite monochromatized Cu Kα radiation (λ = 0.154060 nm), employing a scanning rate of $0.02^{o}\ s^{-1}$ in the 2θ range from 10^{o} to 80^{o}. The field-emission scanning electron microscopy (FE-SEM) images and the energy-disper-

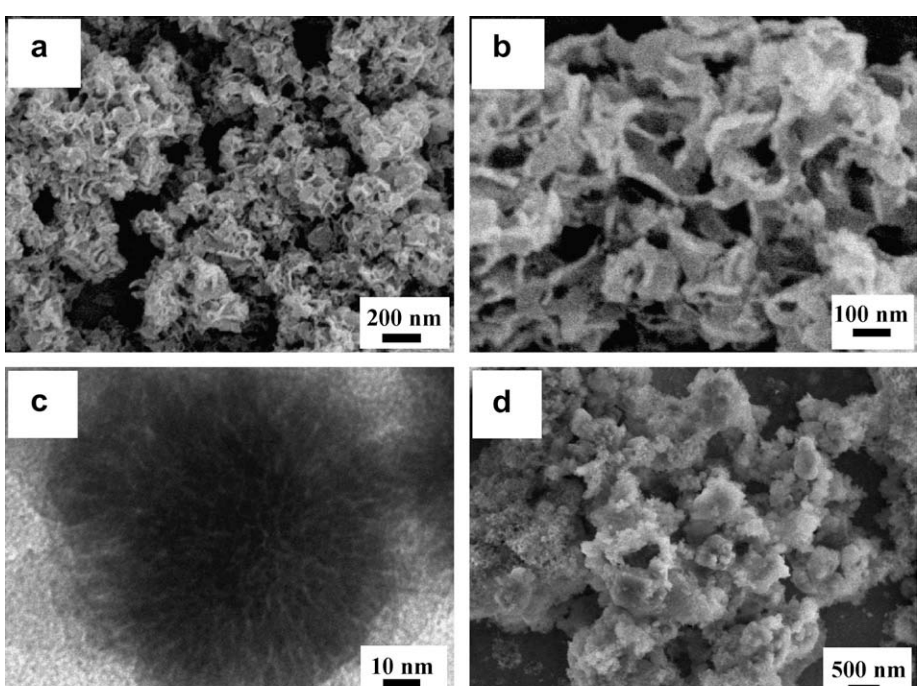

Fig. 2. (a) FE-SEM image of the sample. (b) High-magnification FE-SEM image of the sample. (c) Typical TEM image of an isolated cobalt flower. (d) FE-SEM image of the cobalt catalysts after the fourth cycle in Heck reaction.