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Nanosized Pd assembled on superparamagnetic core–shell microspheres: Synthesis, characterization and recyclable catalytic properties for the Heck reaction

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A B S T R A C T

A series of magnetically recyclable $Pd/Fe_3O_4@\gamma$-Al_2O_3 catalysts were synthesized using the superparamagnetic $Fe_3O_4@\gamma$-Al_2O_3 core–shell microspheres as the supporter and nano-Pd particles assembled on γ-Al_2O_3 shell as the active catalytic component. The structure of the catalysts was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 adsorption–desorption and vibrating sample magnetometer (VSM). The catalytic activity and the recyclability properties of the catalysts for the Heck coupling reaction with aryl bromides and the olefins were investigated. The results show that the microspheres of the magnetic $Pd/Fe_3O_4@\gamma$-Al_2O_3 catalysts were about 400 nm and the nano-Pd particles assembled on γ-Al_2O_3 shell were about 3–4 nm in size. The saturation magnetization (MS) of the magnetic catalysts was sufficiently high to allow magnetic separations. In the Heck coupling reactions, the magnetic $Pd/Fe_3O_4@\gamma$-Al_2O_3 catalysts exhibited good catalytic activity and recyclability. With $Pd/Fe_3O_4@\gamma$-Al_2O_3 (0.021 mol%) catalyst, the bromobenzene conversion and product yield reached about 96.8% and 91.2%, respectively, at 120 °C and in 14 h. After being recycled for six times, the conversion of bromobenzene and the recovery of the catalyst were about 80% and 90%, respectively. The nano-Pd particles were kept well dispersed in the used $Pd/Fe_3O_4@\gamma$-Al_2O_3 catalysts.

1. Introduction

The Heck reaction catalyzed by the noble metal Pd is one of the most important coupling reactions in organic syntheses [1,2]. Homogeneous and heterogeneous Pd catalysts are often used in the Heck reaction. However, homogeneous catalysts are used in less than one fifth of industrial applications due to the facts that the homogeneous catalysts are easily lost after reaction, difficult to separate from the reaction system and certainly costly [3]. Generally, Pd catalysts are initially synthesized as heterogeneous catalysts followed by loading onto active carbon [4], metal oxides [5], zeolites [6,7], polymers [8], or clay [9].

Magnetic catalysts have the incomparable advantages over the traditional catalysts because of their high activity, magnetic recyclability, and reusability. Research on the magnetic nano-catalysts for the Heck reaction had been reported earlier [10,11].

However, due to their high specific surface areas and magnetic properties, magnetic nanoparticles are often easily self-agglomerated [12]. Therefore, SiO_2, C, and metal oxides, polymers are usually used to modify the magnetic nanoparticles and to obtain magnetic nanoparticles with special surface properties that still keep their dispersiveness [13–16]. γ-Al_2O_3 has been used as supporter, adsorbent, and catalyst, owing to its low cost, good chemical stability, high surface area, acidic sites, and controllable synthetic process [17–20]. In the catalytic industry, γ-Al_2O_3 is an ideal supporter. Particularly, the catalysts that are formed by loading the noble metal on the γ-Al_2O_3 were used in organic reactions [20–23]. It is still difficult, however, to separate the catalyst from the liquid phase after the reaction. In our previous research, we found an easy way to synthesize monodispersed Fe_3O_4 [24], which had uniformed diameter. Thus we hypothesized that if we could coat the Fe_3O_4 with γ-Al_2O_3 to obtain core–shell structures, and then load Pd onto the $Fe_3O_4@\gamma$-Al_2O_3 nanospheres, the resulting catalysts would combine their advantages of high activity, excellent mesoporous structure, magnetic recyclability, and reusability.

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In this paper, we illustrated the construction of magnetically recyclable Pd/Fe$_3$O$_4$@γ-Al$_2$O$_3$ nanocomposites possessed the core–shell structure. To evaluate the activity and the stability of the Pd/Fe$_3$O$_4$@γ-Al$_2$O$_3$ nanocomposites, the Heck coupling reactions were chosen as the model reaction. Results showed that the catalyst could be easily separated from the reaction system by employing an external magnetic field, because of the superparamagnetic behavior of Fe$_3$O$_4$. Furthermore, it can be reused for several cycles with sustained selectivity and activity.

2. Experimental

2.1. Synthesis of Fe$_3$O$_4$@γ-Al$_2$O$_3$

Fe$_3$O$_4$ was synthesized according to a slightly modified solvothermal method [24]. Briefly: FeCl$_3$·6H$_2$O (10.8 g), NaAc (28.8 g) and cetyltrimethyl ammonium bromide (CTAB, 0.014 g) were dissolved in 400 mL of glycol under stirring. The obtained homogeneous yellow solution was transferred into a Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated at 200 °C under 400 rpm stirring speed. After heating for 12 h, the autoclave was cooled naturally to room temperature. The obtained black magnetic particles were separated with a permanent magnet, washed with ethanol six times, and dried in vacuum at 60 °C for 24 h.

The obtained Fe$_3$O$_4$ particles (0.1 g) were dispersed in an aluminum isopropoxide (AIP) ethanol solution (60 mL, 0.016 mol/L) under ultrasonication. After 30 min, the solution was transferred to a three-neck flask (250 mL) and stirred for 12 h at 45 °C to obtain the Fe$_3$O$_4$ particles whose surface was saturated with AIP. Subsequently, 50 mL of ethanol/water (5/1, v/v) was added into the solution, and the mixture was allowed to stir for another 1 h to complete the hydrolysis of AIP. Then the mixture was transferred to a Teflon-sealed autoclave and heated at 80 °C for 20 h. The obtained particles were separated with a permanent magnet, washed several times with deionized water and ethanol, and then dried in vacuum at 50 °C for 12 h. After that the products were put into a tube furnace and the system was purged with N$_2$. Then the tube furnace was heated from room temperature to 500 °C (1 °C/min) under the N$_2$ (5 mL/min) ambience, and kept at 500 °C for 4 h. After cooling to room temperature naturally, the Fe$_3$O$_4$@γ-Al$_2$O$_3$ was collected.

2.2. Preparation of Pd/Fe$_3$O$_4$@γ-Al$_2$O$_3$

The obtained Fe$_3$O$_4$@γ-Al$_2$O$_3$ particles (0.1 g) were dispersed in a 2.5 mL PdCl$_2$ aqueous solution (0.6 mg/mL) under ultrasonication. After 30 min, the solution was diluted to 100 mL and transferred to a three-neck flask, stirred for 12 h under 25 °C, separated by a permanent magnet, and finally dried in vacuum at 100 °C for 12 h. The obtained products were put into a tube furnace, which was purged with H$_2$. Then the tube furnace was heated from room temperature to 200 °C (1 °C/min) under the H$_2$ (5 mL/min) ambience, and kept at 200 °C for 3 h. After cooling to room temperature, Pd/Fe$_3$O$_4$@γ-Al$_2$O$_3$ (1.5 wt%) was collected. By changing the volume of PdCl$_2$ added, we synthesized a series of Pd/Fe$_3$O$_4$@γ-Al$_2$O$_3$ catalysts with different Pd loadings in 1.5%, 3.0%, 4.5%, 6.0%, respectively. They were marked as Pd-1, Pd-2, Pd-3, Pd-4, respectively.

2.3. Catalytic reaction

For the Heck reactions, 10 mg of Pd/Fe$_3$O$_4$@γ-Al$_2$O$_3$ catalyst, arylhalide, olefin, dodecane (as an internal standard substance), and base were added to the solvent. The reaction was carried out under reflux condition. The effects of Pd content, solvents,

substrates, and time were investigated individually. The catalyst was collected by an external permanent magnet, and the product was analyzed by gas chromatography (GC). For recycling, the collected catalyst was washed with tetrahydrofuran and separated by an external permanent magnet, then dried under vacuum at 60 °C for 12 h. Then the catalysts were utilized for another run of catalytic testing. Each time, catalyst loss was measured by precision electronic balance.

2.4. Characterizations

The X-ray diffraction (XRD) pattern was collected on a D/Max 2500 VB 2+/PC diffractometer (Rigaku, Japan) with Cu–Kα irradiation (λ = 1.5418 Å, 200 kV, 50 mA) with 2θ values between 10° and 80°. Transmission electron microscopy (TEM) was performed with a JEOL (JEM-2100) transmission electron microscope (JEOL, Japan) operated at 200 kV accelerating voltage. The N$_2$ adsorption–desorption analysis was conducted with an ASAP 2020 M automatic specific surface area and aperture analyzer (MICROMERITICS, USA). Magnetic properties of the samples were measured using a vibrating sample magnetometer (VSM; Lake Shore Model 7400, USA) under magnetic fields up to 18 kOe. The Pd loading amount was determined by inductively coupled plasma mass spectrometry (ICP-MS, SPECTRO ARCOS EOP; SPECTRO Analytical Instruments GmbH, Germany).

3. Results and discussion

3.1. The structure of the catalyst

Fig. 1 shows the crystallinity and phase composition of the samples by X-ray powder diffraction (XRD). The peaks of all samples could be indexed to face center cubic magnetite phase (Fe$_3$O$_4$; JCPDS No. 19-0629). The extra weak diffraction peaks at 45.9°, 66.7° could be indexed to the characteristic diffraction peaks of γ-Al$_2$O$_3$ (2θ = 37.6°, 45.7°, 66.6°; PDF No. 10-425), which indicates that both Fe$_3$O$_4$ and γ-Al$_2$O$_3$ had been obtained [25]. Since the peak at 2θ = 37.6° was so close to the Fe$_3$O$_4$ characteristic diffraction peak that they could not be distinguished by the XRD. Fig. 1 shows that the Pd/Fe$_3$O$_4$@γ-Al$_2$O$_3$ nanocomposites displayed the characteristic diffraction peaks indexed to the Pd (0), which suggested the presence of Pd (0) on Pd/Fe$_3$O$_4$@γ-Al$_2$O$_3$ composites. The intensity became stronger as the concentration of Pd increased.
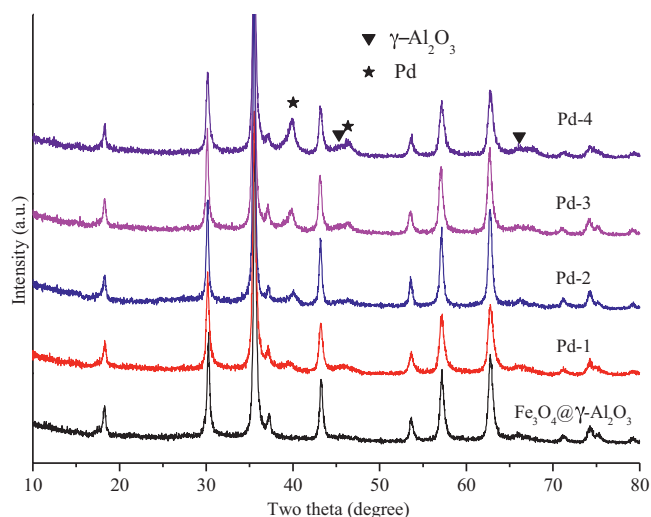

Fig. 1. Wide-angle XRD patterns of Pd/Fe$_3$O$_4$@γ-Al$_2$O$_3$ with different Pd loading.