Magnetite Nanoparticle-Supported Coordination Polymer Nanofibers: Synthesis and Catalytic Application in Suzuki-Miyaura Coupling

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ABSTRACT Functional nanoscale coordination polymers are receiving growing scientific interest because of their potential applications in many domains. In this paper, we demonstrated that a nanofibrous networked metal−organic gel (G1-MNPs) was formed by simply mixing 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)tris(*N*-(pyridin-3-ylmethyl)benzamide) (L) and Pd(COD)$(NO_3)_2$ in $CHCl_3$-MeOH with a Pd/L molar ratio of 1:1 in the presence of magnetite nanoparticle (MNPs). The self-assembly behavior of nanofibers was not significantly effected by the introduction of magnetite nanoparticles. The xerogel of G1-MNPs was superparamagnetic and showed catalytic activity in Suzuki-Miyaura C−C coupling reactions. The Pd(II) xerogel could be magnetically isolated and recycled with a permanent magnet. It represents a novel strategy to introduce nanoparticles into functional coordination polymers for multifunctional materials.

KEYWORDS: metal−organic gel • Pd • C−C coupling • multifunctional material

INTRODUCTION

Functional nanoscale coordination polymers, made from metal ions connected by organic ligands, have received growing attention because of their potential applications in different domains including biological sensing, drug delivery, photoluminescence, and catalysis (1, 2). Among these nanomaterials, nanofibrous coordination polymers are relatively scarce and particularly interesting (3, 4). The metal−organic gel nanofibers have been shown to be efficient and promising catalysts (5), partly because the nanofiber catalysts are self-supported and recycled (6), and result in enhanced efficiency because of their well-ordered arrangement of catalytically active sites (7).

Magnetic nanomaterials are of interest because of their unique physical properties. Superparamagnetic nanoparticles have advantages including easy preparation and functionalization, low toxicity and price (8−10). Superparamagnetic materials can be removed and recycled from the solution by applying an external magnetic field and dispersed readily after removing the magnetic field. The catalyst supported on superparamagnetic nanoparticles can be easily separated from the reaction mixture and products by simple magnetic attraction and reused. As a result, filtration or centrifugation is not required for catalyst recovery and recycling, which is sometimes cumbersome, e.g., in the case of air-sensitive reactions. Recently, Arai et al. and Sweigart et al. have successfully constructed Cu(II), Mn(II), and Cd(II) coordination polymers on the surface of magnetic nanoparticles (11). The resulting Cu(II) nanospheres show both the properties of magnetic nanoparticles and coordination polymer catalyst, which can be recovered by magnetic separation in the aerobic oxidation of silyl enolates (11a).

In the course of our research on metal−organic gel catalysis (4, 12), we have examined the use of metal−organic gels based on 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)tris(*N*-(pyridin-3-ylmethyl)benzamide) (L, Scheme 1) and Pd(COD)$(NO_3)_2$ (COD = cycloocta-1,5-diene) as catalyst in Suzuki-Miyaura coupling (4). The fibrous networked metal−organic gel (G1) was formed when the molar ratio of Pd/L is 1:1 and had improved catalytic activity, suggesting that nanofibers are potentially interesting catalytic materials. Herein we wish to report a simple one-pot synthesis of magnetically separable gel nanofiber catalyst (Scheme 1). The Pd(II) coordination polymer gel nanofibers bases on G1 were supported on superparamagnetic magnetite (Fe_3O_4) nanoparticle (MNPs). The approach combines both the characteristics of nanofiber catalyst and MNPs, which offers a new solution for recycled nanoscale coordination catalysts.

EXPERIMENTAL SECTION

Materials and Methods. All starting materials and solvents were obtained from commercial sources and used without further purification. 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)tris(*N*-(pyridin-3-ylmethyl)benzamide) (L) was prepared according to previously published procedure (4). Infrared spectra were measured on a Nicolet Avatrar 330 FT-IR spectrometer with KBr pellets. A Lakeshore 7404 vibrating sample magnetometer was used to obtain the magnetization curve at room temperature.

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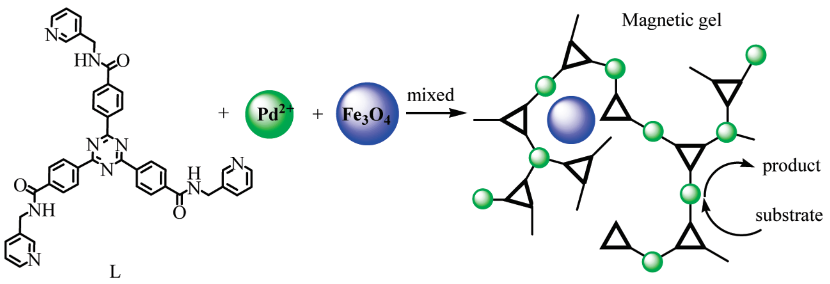
Scheme 1. Schematic Representation of Magnetic Gel Nanofibers for Organic Transformation



The variable-temperature magnetic-susceptibility data were measured with a Quantum Design MPMS7 SQUID magnetometer. The measurements were performed on the sample of crushed xerogel g1-MNPs (0.0281 g) in the range of 5−360 K range and the magnetization was measured in a 500 Oe dc field. The TGA analyses were carried out on a Netzsch Thermo Microbalance TG 209 F3 Tarsus analyzer. Pd analyses were performed by inductively coupled plasma atomic emission spectroscopy using a TJA IRIS HR ICP instrument. Transmission electron micrographs (TEM) were recorded on a JEOL JEM-2010HR microscope. Field-emission scanning electron micrographs (FE-SEM) were recorded by using a Jeol JSM-6330F instrument after gel samples were dispersed in ethanol and slowly evaporated to dryness in air. Prior to examination, the xerogels were dried in a vacuum and coated with a thin layer of gold.

Preparation of Fe_3O_4 MNPs. Fe_3O_4 MNPs were prepared by the coprecipitation method (13). $FeSO_4 \cdot 7H_2O$ (3.06 g, 0.011 mmol) and $FeCl_3 \cdot 6H_2O$ (5.41 g, 0.02 mmol) were mixed in an aqueous solution (100 mL). $NH_3 \cdot H_2O$ was added into the mixture to adjust the pH value to 9 while vigorous stirring. The resulted mixture was kept at 70 °C for 45 min. MNPs thus synthesized were separated from the solution with a permanent magnet and washed several times with water until the pH value was 7. The aqueous layer was decanted to yield black MNPs. To the Fe_3O_4 MNPs, polyethylene glycol (30 mL, M = 400 g mol^{-1}, aqueous solution, 150 g L^{-1}) was added. The suspension was stirred vigorously for 3 h at 60 °C, and then separated using a magnet. The solvent and the nonmagnetic suspension were decanted to obtain modified MNPs. The modified NMPs were dispersed in H_2O, MeOH or EtOH (65 mL), sonicated for 15 min, and stirred for 12 h, yielding water-, methanol-, or ethanol-dispersed MNPs. The content of Fe_3O_4 nanoparticles was determined to be 34 mg mL^{-1}.

Preparation of G1-MNPs. 0.05 mL of methanol-dispersed MNPs was added dropwise to a solution of L (28.4 mg) in $CHCl_3$/MeOH (1 mL/0.95 mL) and the mixture was sonicated for 5 min. $Pd(COD)Cl_2$ (11.4 mg) and $AgNO_3$ (13.6 mg) were mixed in MeOH (2 mL) and stirred for 10 min, followed by filtration to remove AgCl to obtain a methanolic solution of $Pd(COD)(NO_3)_2$. Two solutions were mixed rapidly and allowed to stand. A light coffee gel (G1-MNPs, 7%) was formed after about 2 min. The gel was stable in MeOH while stirring.

General Procedure for Suzuki Coupling. R-C_6H_4-X (0.5 mmol), phenylboronic acid (1.5 equiv), Na_2CO_3 (3 equiv), xerogel catalyst (1 mol % of Pd(II)), and 6 mL of CH_3OH were added to a flask equipped with a magnetic stirring bar. The reaction mixture was stirred at 60 °C under ambient atmosphere. After the reaction, the catalyst was separated with a permanent magnet and washed with Et_2O. The collected xerogel was dried and reused for the next run. The resultant reaction mixture was added to H_2O and extracted with Et_2O. The organic layer was analyzed by GC-MS and NMR spectroscopy.

General Procedure for Heck Coupling. R-C_6H_4-X (1 mmol), alkene (2.0 equiv), Na_2CO_3 (1.5 equiv), xerogel catalyst (1 mol % of Pd(II)), and 5 mL of *N*,*N*-dimethylformamide (DMF) were added to a flask equipped with a magnetic stirring bar. The reaction mixture was stirred at 140 °C under ambient atmosphere. After the reaction, the catalyst was centrifuged for recovering. The resultant reaction mixture was added to H_2O and extracted with Et_2O. The organic layer was analyzed by GC-MS and NMR spectroscopy.

RESULTS AND DISCUSSION

Gelation of Magnetite Nanoparticles. Magnetite nanoparticles were prepared by coprecipitation of Fe(III) and Fe(II) ions in a basic solution. The obtained MNPs were subsequently modified with polyethylene glycol (PEG) in order to get water-, methanol-, or ethanol-dispersed MNPs. The methanol-dispersed MNPs were readily mixed with L in $CHCl_3$/MeOH with sonication. Treating this MNPs-containing solution with a methanolic solution of $Pd(COD)(NO_3)_2$ gave a light coffee metal−organic gel after 2 min in the Pd/L molar ratio of 1:1. Formation of the MNPs-containing gel was confirmed by turning the sample upside down. Heating of the gels could not transform the gel into solution, revealing they are thermally irreversible. Different contents of MNPs varying from 4 to 50% (mass fraction, the amount of MNPs divided by the total gelator mass) could be successfully loaded in the metal−organic gel G1 with slightly increasing gelation time from 2 to 5 min (Figure 1). The gel containing 7% of MNPs could respond effectively to the external magnetic field and was used for the following studies as a typical gel. This represents a remarkably simple preparation of magnetic catalysts self-assembled quantitatively from organic ligand and metal ion.

FT-IR was used to characterize organic functionalities of the xerogel of G1-MNPs (referred to as g1-MNPs) (Figure 2). FT-IR spectrum of g1-MNPs is similar to that of the xerogel of G1 (g1). The broad bands at ca. 3300−3400 cm^{-1} indicated the hydrogen bonding present in g1-MNPs. The

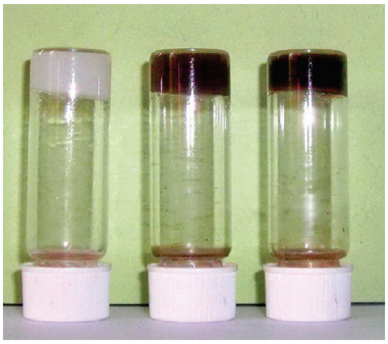


FIGURE 1. Photographs of G1 (left), G1-MNPs (4%) (middle), and G1-MNPs (7%) (right) for comparison.

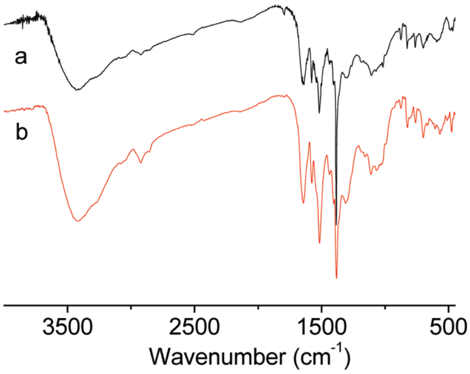


FIGURE 2. IR spectra (KBr pellets) of (a) g1 and (b) g1-MNPs for comparison.

vibration at 1644 cm^{-1} is due to the amide C=O band, and strong bands at 1577−1516 cm^{-1} result from combined N−H deformation and C−N stretching vibrations. The NO_3^- band is present as an intense peak at 1382 cm^{-1}. The characteristic Fe−O vibration at approximately 589 cm^{-1} could not be identified probably due to the low content of Fe_3O_4 nanoparticles. The surface analysis by XPS confirmed the presence of Pd and Fe in a powder sample of g1-MNPs (see Figure S3 in the Supporting Information). The signals at 338.8 and 337.5 eV in the Pd $3d_{5/2}$ region revealed coordination of Pd(II) to the ligand (14). The spectrum showed a signal at 711.6 eV in the Fe $2p_{3/2}$ region confirming the presence of Fe_3O_4.

Scanning electron microscopy (SEM) images of the xerogel g1-MNPs display a nanofibrous networked morphology (Figure 3a,b), which is closely similar to the xerogel g1 (4). The thread ball-like network was consisted of nonofibers with a diameter of about 30 nm. Transmission election microscopy (TEM) confirms that the magnetic xerogel is composed of interconnected nanofibers with an average diameter of about 30 nm (Figure 3c,d). Compared with the xerogel g1 (Figure 3e,f), the nanofibers of g1-MNPs have similar sizes and Fe_3O_4 nanoparticles are clearly located in the xerogel g1-MNPs (Figure 3c,d). Most of the Fe_3O_4 nanoparticles are embedded in the fibers with a diameter of around 5 nm. In addition, loading of up to 50% MNPs resulted in the formation of gel nanofibers with similar sizes (see Figure S1 in the Supporting Information). Consistent with the EM results, the material showed no obvious adsorption using N_2 gas as the adsorbate at liquid nitrogen temperature. The results thus indicate the presence of the Fe_3O_4 nanoparticles had little effect on the self-assembly behavior of gel nanofibers, which results from oligomerization or polymerization through coordinative interactions between Pd(II) ion and the pyridine N donor in G1-MNPs revealed by NMR and others (4). This observation is consistent with the previous results for an organogel by McPherson et al. (15).

The magnetization curve of g1-MNPs were determined using a vibrating sample magnetometer (Figure 4a). The absence of magnetic hysteresis at 300 K suggests the superparamagnetic behavior of the magnetite nanoparticles included in the material. The saturation of the magnetization could be observed with applied magnetic fields above 3000 G, and the saturation magnetization from the hysteresis loop was found to be 3.2 emu g^{-1}. The saturation magnetization is about 6.3% of the bare magnetite, which is consistent with the presence of about 7% MNPs in the gel during preparation. It means that the net magnetization of the particle assemblies is zero in the absence of an external field, and the magnetization of the particles aligns with the field direction and reaches the saturation magnetization under a large external field. The temperature dependence of g1-MNPs under an external applied magnetic field of 500 Oe is illustrated in Figure 4b in the form of magnetization versus temperature. Above the blocking temperature of the magnetic material, the magnetization decreases steadily with rising temperature.

Thermogravimetric analysis of the xerogel g1-MNPs revealed two weight losses of 5.7% and 16.3% in the temperature of RT-110 and 110−320 °C, respectively. The continuous loss of weight may be attributed to the loss of the solvents and organics absorbed on the particle surface and those physisorbed and chemisorbed in the nanofibers (Figure 5), since there were several organic components present in the g1-MNPs nanofibers including polyethylene glycol, COD, and organic solvents. The coordination network may be anticipated to collapse above 320 °C.

Catalytic Activity of g1-MNPs. The gel G1-MNPs was assessed for its catalytic activity in two types of carbon−carbon bond formation reactions, Suzuki and Heck reactions. The gel was slowly evaporated to dryness in air and was dried in vacuum for 20 h prior to catalytic study. The results for Suzuki coupling were summarized in Table 1. The xerogel g1-MNPs showed better activity in MeOH at 60 °C (nearly quantitative yield after 2 h) than that in MeOH at r.t. or in H_2O at 80 °C in the coupling of iodobenzene and phenylboronic acid. It was observed that iodobenzene or 4-bromoacetophenone (an electron-deficient aryl bromide) gave the biaryls in higher yields than bromobenzene or 4-bromoanisole (an electron-rich aryl bromide). The catalytic activity had no obvious change after loading of magnetite nanoparticles compared with that of the nonmagnetic gel. It suggests that the MNPs-modified xerogel and the nonmagnetic xerogel had closely related coordinate modes in the molecular level. Because of their thermally irreversible nature, the xerogel could not recover its original wet gel morphology after swelling in the reaction solution. The xerogel were observed to be insoluble and dispersed in the reaction system as fine particles.

The recyclability of the MNP-supported gel catalyst was studied in Suzuki coupling. The recyclability of the xerogel g1-MNPs was examined for the reaction of iodobenzene with phenylboronic acid as a model reaction. After the completion of the reaction, the xerogel catalyst was separated by a permanent magnet, washed with H_2O and Et_2O to remove residual product, dried, and subjected to the next run (Figure 6). Interestingly the xerogel survived efficient stirring and was shown to be readily recyclable up to four runs without significant loss of activity, affording the products in 99, 95, 92, and 94% yields, respectively (Table 2).

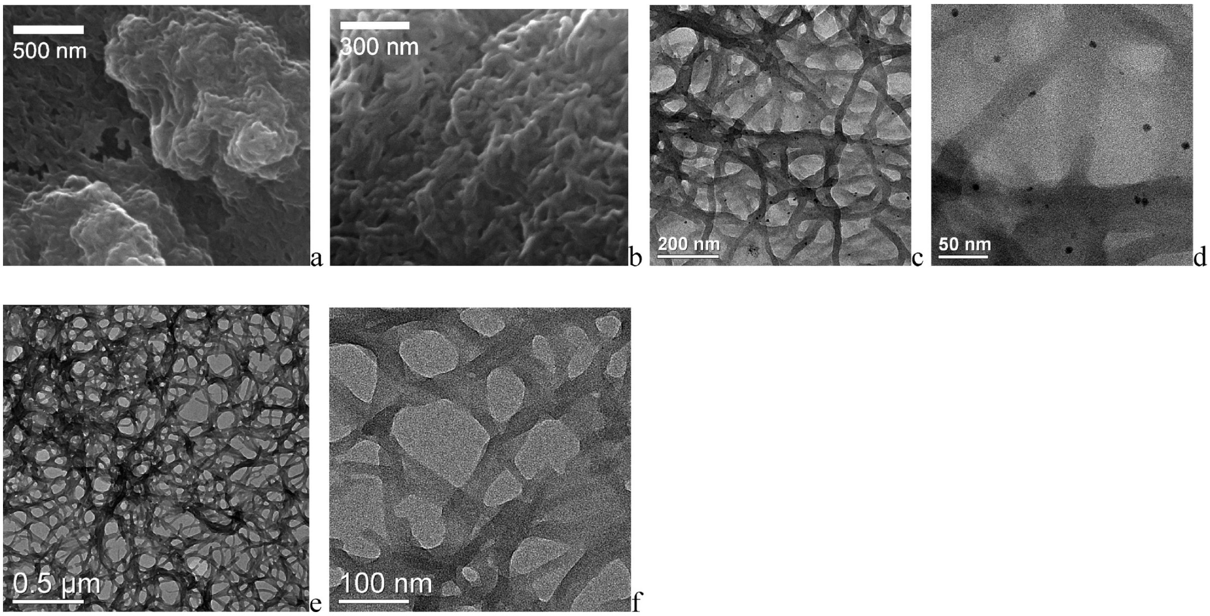


FIGURE 3. (a, b) SEM images and (c, d) TEM images of g1-MNPs; (e, f) TEM images of g1.

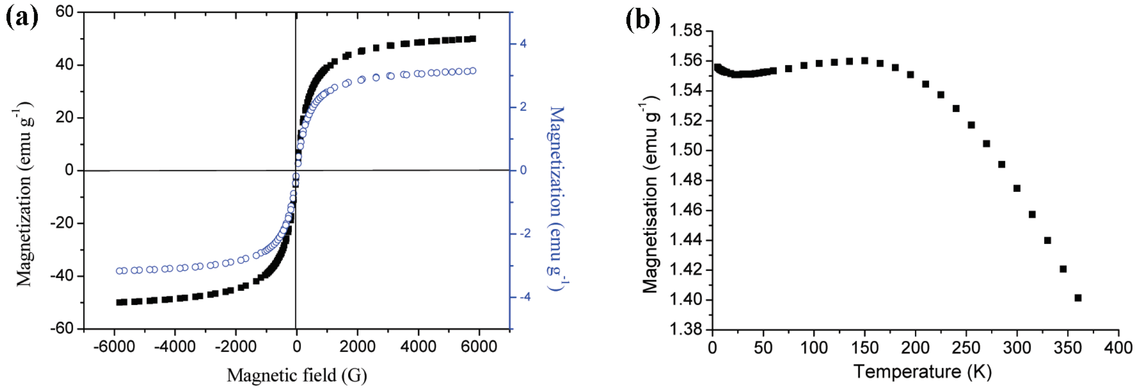


FIGURE 4. (a) Field-dependent magnetization curve of the bare modified Fe_3O_4 nonoparticles (black, square) and the xerogel g1-MNPs (blue, circle) at 300 K. (b) Plot of magnetization versus temperature for the xerogel g1-MNPs at an applied field 500 Oe.

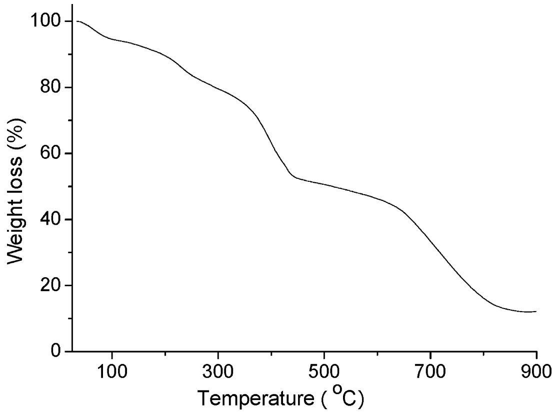
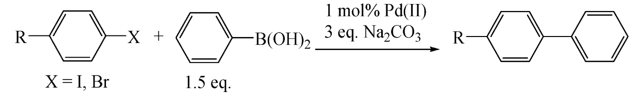


FIGURE 5. TG curve of g1-MNPs.

Table 1. Suzuki Cross-Coupling of Aryl Halides and Phenylboronic Acid in the Presence of G1-MNPs As Catalyst



entry	X, R	*T* (°C)	solvent	yield (%)[a] (time (h))
1	X = I, R = H	RT	MeOH	73 (2.0)
2	X = I, R = H	60	MeOH	96 (1.5), >99 (2.0)
3	X = I, R = H	80	H_2O	58 (4.0)
4	X = Br, R = H	60	MeOH	59 (0.5), 78 (1.0), 89 (5.0)
5	X = Br, R = OMe	60	MeOH	27 (0.5), 29 (4.0)
6	X = Br, R = COMe	60	MeOH	97 (0.25), 98 (0.5)

[a] GC yield.

To clarify whether the catalysis is heterogeneous or homogeneous, we performed the conventional filtration test; it showed that the yield of product did not change after removal of the xerogel catalyst. In addition, ICP-AES analysis revealed no detectable Pd in the filtrate. These observations may support that it is a heterogeneous reaction. TEM analysis of the catalyst indicated that interconnected nanofibers with a diameter of around 4 nm were observed after the third use (Figure 7). It suggests that the original gel nanofibers changed in the reaction. The change might be attributed to possible composition of the original nanofibers of thinner fibers and/or the catalytic cycle happening in the reaction (16). However, because very limited data of the morphology of nanoscale coordination polymers after ca-

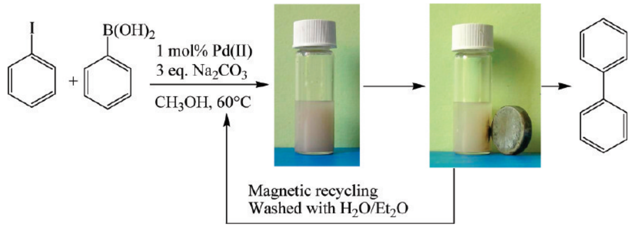


FIGURE 6. Photographs of a reaction mixture containing g1-MNPs before and after magnetic separation showing all the black xerogel was concentrated on the side wall of the flask by a permanent magnet (the observed white suspension is due to undissolved Na$_2$CO$_3$).

Table 2. Reuse of Catalyst in Suzuki Reactions of Iodobenzene and Phenylboronic Acid Catalyzed by the Xerogel g1-MNPs[a]

	run				
	first	second	third	fourth	fifth
GC yield (%)[b]	99	99	95	92	94

[a] Conditions: PhI (0.5 mmol), PhB(OH)$_2$ (0.75 mmol), catalyst (1 mol % of Pd(II)), Na$_2$CO$_3$ (1.5 mmol), CH$_3$OH (6 mL) at 60 °C, for 2 h under an air atmosphere. [b] Determined by GC.

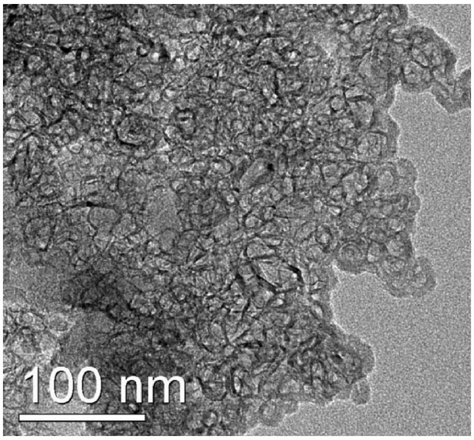


FIGURE 7. TEM image of g1-MNPs after the third use.

talysis are available, explanation of such an unprecedented morphology change needs further investigation.

The gel catalyst was also employed as catalyst in the Heck arylation of alkenes with aryl halides (see Table S1 in the Supporting Information). In the presence of a catalytic amount of xerogel (1 mol % Pd), the arylation reaction of alkenes (styrene, acrylic acid, or methyl acrylate) with iodobenzene could take place at 140 °C and the desired products were obtained in satisfied yields (>95%) after 1 h. The arylation reactions of 4-bromoacetophenone (having electron-withdrawing substituent) with methyl acrylate afforded nearly quantitative yield after 4 h of reaction time. As expected, the arylation reaction of methyl acrylate with deactived bromobenzene afforded a poor yield of 16% after 2 h. It is to note that the magnetism decreased after the first use for the Heck coupling of iodobenzene and styrene. TEM showed that the magnetite nanoparticles may aggregate and the xerogel morphology changed after the reaction at high reaction temperature (140 °C) (see Figure S4 in the Supporting Information). After the second run the magnetism changed significantly and it could not be recovered by magnetic attraction any more, although a good yield of 90% was obtained. However, the catalyst could still be recovered by filtration as previously shown for the nonmagnetic gel in Suzuki reactions (4).

CONCLUSIONS

In summary, superparamagnetic MNPs-supported gel nanofibers have been synthesized by simply mixing the metal ion and organic ligand in the presence of the MNPs. The self-assembly behavior of nanofibers was not significantly effected by the introduction of magnetite nanoparticles. The gel nanofibers had similar sizes and catalytic activity with the nonmagnetic nanofibers for Suzuki-Miyaura C−C coupling reactions arising from its Pd(II) center. The resulting nanofiber catalyst was easily attracted to an external magnetic field and it could be reused up to four times without significant degradation in activity in the coupling of iodobenzene with phenylboronic acid. Although the catalytic activity of present gel system is routine for Pd(II) catalysis, it demonstrates a new strategy to introduce nanoparticles into functional coordination polymers through one simple step for multifunctional materials.

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Supporting Information Available: Additional SEM and TEM images and catalytic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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