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A brand-new catalytic system: a Pd-based catalyst directly attached on the inner walls of the reactor which independently catalyzed the Heck reaction[†]

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A Pd-based catalyst directly attached on the inner surface of the reactor as a new catalytic system has been achieved and developed *via* an electrospinning technique followed by an impregnation–reduction and a simple carbonization process. The application of the reactor was demonstrated using the Heck reaction. This work showed many potential advantages in numerous fields.

Carbon-carbon cross-coupling reactions are among the most useful and most widely studied synthetic transformations. One of the most important processes, the Heck coupling reaction, has been abundantly used in syntheses and widely studied in recent decades.1-5 Palladium is the metal of choice for these reactions and several catalysts rely on Pd(II) and Pd(0) species, mostly in the form of Pd complexes.6 Transition metal nanoparticles (NPs) are particularly attractive, finding significant applications in optics,7 electronics,8 and especially in catalysis.9-11 It is well believed that a high efficiency in catalysis often requires nanometric and uniform size as well as a homogeneous distribution of the catalyst throughout a suitable substrate. Moreover, preventing nanoparticles from aggregation is one of the most important issues for preserving their properties. In this respect, Pd NPs are widely utilized as a catalyst for C-C cross-coupling reactions, as witnessed by the numerous reviews present in the literature.12

However conventional homogeneous palladium catalysts have some disadvantages in separation and recovery that limit the industrial and synthetic applications of the Heck reaction. In recent years, immobilizing metal catalysts onto solid supports has received great attention.¹³ A variety of organic and inorganic supports have been reported¹⁴⁻¹⁶ and among them, nanofibers prepared though the electrospinning technique turn out to be the simplest and ideal supports.¹⁷⁻¹⁹ Our previous research²⁰ reported our findings in electrospinning mixtures of polyacrylonitrile (PAN) and palladium chloride (PdCl₂) to form PAN-PdCl₂ fibers. The fibers was followed by an impregnation– reduction and subsequent calcination methods, so the Pd salt attached to the PAN was reduced to Pd nanoparticles and our group has previously demonstrated that this kind of catalyst exhibited excellent catalytic activity for the Heck reaction.

Therefore a stable catalytic system making use of supported Pd NPs would undoubtedly allow the Heck reaction to be carried out. In this way, herein, we designed a unique catalytic reactor to develop a brand-new catalytic system. To the best of our knowledge, this is the first report that directly electrospun PAN-PdCl₂ fibers to the inner surface of the reactor and the catalyst can attach to the reactor firmly even suffering reduction, preoxidation and carbonization processes. The effectiveness of this catalytic system is demonstrated for the Heck coupling of iodobenzene with acrylates. This work opens the door to the development of a novel catalytic system and the inspired Pd materials are active with a variety of substrates, suggesting that the system is versatile and may translate to various other chemical reactions.

The digital photos of the reactor are shown in Fig. S1.[†] The entire reactor that was designed consists of two parts: the bottom of the reactor was used for the collection of the catalyst and the top part was equipped with a thermometer and condenser tube. The two parts were fixed and rotated by a screw opening. Scheme 1 shows all of the steps for the preparation of three types of catalyst. Firstly, we directly electrospun PAN-PdCl₂ fibers to the inner surface of the reactor, followed by a process of NH₂NH₂ reduction, in which most of the Pd²⁺ ions can be reduced to Pd(0). After that, the reactor was placed in a tube furnace at 250 °C in air for two hours to prepare the Pd/ PANOF catalyst. In the same way, we obtained the Pd/LTCF-350 and Pd/LTCF-450 catalysts as follows: 250 °C annealing for 2 hours in air; heating up to 350 °C and 450 °C at a rate of 2 °C min⁻¹ and annealing for 2 hours in nitrogen. Finally, we added the reactants of the Heck reaction, reacted at the specific temperature and time.

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Scheme 1 Schematic illustration of the preparation of three types of catalyst.

Fig. S2[†] shows the FTIR spectra for the PAN/PdCl₂ fibers, Pd/ PAN fibers after the hydrazine hydrate solution treatment, and Pd/PANOF, together with Pd/LTCF-350 and Pd/LTCF-450. Fig. S2A and B[†] show the electrospun PAN/PdCl₂ composite nanofibers before and after the hydrazine hydrate solution treatment with the characteristic bands of the nitrile (2237 cm⁻¹) groups coming from the polyacrylonitrile comonomer. The characteristic peak at around 2927 cm⁻¹ for CH₂ confirms methylene, and the triplet at 1099 cm⁻¹ represents the C-CN group. At the same time, in Fig. S2C-E,† the thermal treatment resulted in the essential disappearance of the nitrile (2237 cm^{-1}) groups. That means, the structure of PAN had changed, the linear PAN molecular chain structure could have been converted into the aromatic ladder structure after the thermal treatment.²¹ The absorption peaks at 1620 cm⁻¹ for the C=N bonds, and at 1377 and 758 $\rm cm^{-1}$ for the C=C-H group appeared, presumably due to the dehydrogenation.

A comparison of the UV-vis spectra of the samples is displayed in Fig. S3.† The red spectrum (Fig. S3A†) presented for the PdCl₂/PAN fibers displays a feature absorbance band at 244 nm. This absorbance is likely due to the interaction between the Pd²⁺ and the polymer.^{22,23} Upon reduction, represented by the black spectrum (Fig. S3B†), this band disappeared with the formation of a broad absorbance characteristic of nanoparticle formation, indicating that bivalent palladium was reduced to zerovalent palladium.²⁴

As shown in Fig. 1A and B, the electrospun $PAN/PdCl_2$ composite nanofibers before and after the hydrazine hydrate solution treatment align in random orientations and interweave to form a fibrous film. The surface of the $PAN/PdCl_2$ nanofibers was smooth and their average fiber diameters were uniform within 150 nm, after the hydrazine hydrate solution reduction, the morphology of the nanofibers almost did not change, the average diameters of nanofibers shrunk to 130 nm. Also, the fibrous character of these fiber mats was still retained. The inset section gave us visual evidence that the nanofibers could firmly attach onto the inner surface of the reactor, or even suffer a liquid reduction process.

Upon further treatment with different temperatures of 250 °C (Fig. 2A1), 350 °C (Fig. 2B1) and 450 °C (Fig. 2C1), these fibers appeared to be slightly smaller with average diameters of 110–150 nm, which is likely due to the thermal treatment. Nevertheless, the fibrous character of the fibers was still retained at all stages. TEM images demonstrate that with the increase of the carbonization temperature,



Fig. 1 SEM images of (A) $PAN/PdCl_2$ nanofibers and (B) Pd/PAN nanofibers obtained after they were reduced by NH_2NH_2 and taken from the inner surface of the reactor; the inset shows corresponding digital photos.

Pd/PANOF (Fig. 2A2), Pd/LTCF-350 (Fig. 2B2) and Pd/LTCF-450 (Fig. 2C2) there were no obvious changes in the sizes of Pd NPs. They were roughly spherical in shape and were randomly distributed on the surface of the nanofibers with a moderate density and their average sizes were 3.8 nm, 5.3 nm, and 3.71 nm, respectively. The Pd NPs were stabilized in place even after the Heck reaction mechanism thus allowing for efficient reuse in subsequent steps and this finding was in accord with the next discussion in Fig. S4.[†]

As shown in Fig. 3, their X-ray photoelectron spectroscopy (XPS) spectra possess three peaks centered at 284.9, 400.02, and 532.1 eV, corresponding to C 1s, N 1s, and O 1s, respectively (Fig. 3A). PAN is a nitrogen-rich precursor, and the presence of nitrogen species facilitates the loading of Pd nanoparticles onto the support and enhances the capacity for adsorbing metal ions in aqueous solution, due to the binding between nitrogen species and metals usually making them hard to remove during thermal treatment.²⁵ The high-resolution N 1s peak in the XPS spectra is displayed in Fig. 3B. The signals at 400.4 eV are assigned to the pyridine type nitrogen. However, another new



Fig. 2 SEM images of Pd/PANOF (A1), Pd/LTCF-350 (B1) and Pd/LTCF-450 (C1); the insets provide the corresponding digital photos. TEM images of Pd/PANOF (A2), Pd/LTCF-350 (B2) and Pd/LTCF-450 (C2); the insets show the size distribution histograms, respectively.

peak which appears at 398.4 eV in Fig. 3B3 is assigned to the pyridine nitrogen. This is mainly because the samples obtained at 450 °C are not fully conductive, indicating that aromatization is not completed at that temperature but had already occurred partially.²⁶ The XPS spectrum in the Pd 3d region of Pd/PANOF (Fig. 3C1), Pd/LTCF-350 (Fig. 3C2) and Pd/LTCF-450 (Fig. 3C3) indicated the presence of a mixture of Pd(0) and Pd(π) as is evident from the measured binding energy of the Pd 3d^{5/2} and 3d^{3/2} electrons at 335.1 and 340.1 eV for Pd(0) and 338.1 and 343.3 eV for Pd(π), respectively.

Upon confirmation of the fabrication of Pd metallic nanoparticles, the catalyst and system were studied for catalytic reactivity for the formation of C–C bonds. Specifically, we focused on the Mizoroki–Heck cross-coupling reaction and this reaction was selected for two specific reasons. First, the final organic product of the catalytic reaction possesses a newly formed C–C bond, which is important for a vast variety of fields. Second, many of the reagents, both aryl halides and alkenes, are commercially available to be used for facile characterization of the reactivity of the newly produced Pd based reactor system. Additionally, the solubility of the reagents and the stability of the system can be tailored to fit a variety of solvent polarities and reaction conditions, thus facilitating a broad set of analyses of the Pd nanomaterial catalytic activity.

For the catalytic analysis of the system, relatively mild conditions were initially employed for the coupling of iodobenzene with *n*-butyl acrylate. For this reaction and system, 1 mmol iodobenzene was co-dissolved in a solvent with 1.5 mmol of acrylates. This solution was added directly to the reactor and the reaction was left for 24.0 h with no stirring. The temperature of the system was 100 $^{\circ}$ C instead of boiling point.

The solvent effects for the Heck coupling of iodobenzene with *n*-butyl acrylate in four different solvents are summarized in Table 1. Examination of Table 1 shows that DMF is the efficient solvent for the Pd/PANOF catalyzed cross-coupling reaction.



Fig. 3 (A) The X-ray photoelectron spectra for Pd/PANOF, Pd/LTCF-350 and Pd/LTCF-450; (B) N 1s spectra; (C) Pd 3d spectra.

Table 1 Solvent effect on the Heck reaction

Entry	Solvent	Conversion ^{b} (%)	Selectivity ^b (%)	
1	EG	8.67	2.25	
2	DMF	95.55	79.94	
3	DMSO	94.21	74.39	
4	Toluene	27.09	26.66	

 a Reaction conditions: iodobenzene (1 mmol); *n*-butyl acrylate (1.5 mmol); triethylamine (3 mmol); catalyst: Pd/PANOF in 10 mL solvent; temperature: 100 °C; reaction time: 24 h. b Determined from the GC analysis.

A series of bases were examined for the cross-coupling reaction and the related results are summarized in Table S1.† Examination of entries 1–3 of Table S1† shows that inorganic bases (either strong alkalis or weak inorganic salts) scarcely promote the Heck reaction in this catalytic system whereas the organic base (triethylamine) is able obviously to enhance. It is not difficult to explain, as the system of the solvent is DMF and this kind of organic solvent is almost insoluble for all three inorganic bases. As a result, the function of the bases is much weaker than the organic base. So triethylamine is an optimal choice of bases.

The most advantageous aspect of this system is that the catalyst attached on the surface of the reactor can be readily recycled from the reaction media by simple washing even with no need for filtration and then reused for the subsequent studies. The Pd-based catalyst together with the reactor builds up an overall catalytic system and independently catalyzes the Heck reaction. The recyclability of all three catalysts was examined (Table 2). All three types of catalysts presented high catalytic activities in the first three runs. However, a considerable decrease in the catalytic activity was observed after it was reused four times. We examined the samples by TEM after the 4th run (Fig. S4[†]) and found an amount of the Pd nanoparticles fell off the fibers. A comparison of the activities of three catalysts indicated that the activities of Pd/PANOF catalyst had dropped significantly and this may be mainly because the polyacrylonitrile preoxidated fiber (PANOF) did not undergo a process of carbonization and therefore some active groups still existed on the fibers that led to the loss of the Pd NPs during the reaction. This finding agrees with the FTIR analysis in Fig. S2.[†] As the carbonization temperature rises, the properties of the catalyst from preoxidated fiber gradually converts to carbon fibers and therefore the Pd/LTCF-450 type catalyst presents more stability after four cycles as expected. Additionally, it is also noteworthy that a small part of the catalyst fell off the reactor during the reaction and washing process and this was another reason for the dropping of the catalytic activities.

As shown from the recycling experiments, the Pd/LTCF-450 catalyst exhibited a better catalytic activity and recyclability than the other two catalysts. So we chose the Pd/LTCF-450 catalyst to further investigate the Heck reaction using iodobenzene with different olefin substrates. However, a lower selectivity was found for the cross-coupling reaction of

 Table 2
 Repeated uses of three types of catalyst in the Heck reaction^a

Run	Pd/PANOF		Pd/LTCF-350		Pd/LTCF-450	
	Conversion ^{b} (%)	Selectivity ^{b} (%)	Conversion ^{b} (%)	Selectivity ^{b} (%)	Conversion ^{b} (%)	Selectivity ^{b} (%)
1	95.55	79.94	94.03	88.88	99.34	69.86
2	90.04	84.88	87.70	92.50	100	71.95
3	89.89	75.18	90.89	60.74	100	72.70
4	64.56	67.28	71.13	61.29	81.26	73.26

^{*a*} Reaction conditions: iodobenzene (1 mmol); *n*-butyl acrylate (1.5 mmol); triethylamine (3 mmol); solvent 10 mL DMF; temperature: 100 °C; reaction time: 24 h. ^{*b*} Determined from the GC analysis.

 Table 3
 Heck reaction of iodobenzene with different substrates^a

Entry	R	Product	Conversion ^{b} (%)	Selectivity ^b (9
1	$C_2H_3O_2$	Contraction of the second seco	96.53	96.06
2	$C_3H_5O_2$	Contraction	100	72.64
3	$C_5H_9O_2$		99.34	69.86
4	CHO_2	Он	98.39	37.33
5	CN	N	92.30	73.10

 a Reaction conditions: iodobenzene (1 mmol); substrates (1.5 mmol); triethylamine (3 mmol); solvent 10 mL DMF; temperature: 100 °C; reaction time: 24 h. b Determined from the GC and GC-MS analysis.

iodobenzene with acrylic acid, presumably due to the stereohindrance effect that produced by-products (Table 3).

TEM images of the three catalysts after the 4th run (Fig. S4[†]) show that the morphology and size of the palladium NPs after four cycles had better uniform dispersion and no significant agglomeration. Their average sizes are 4.06 nm, 5.34 nm, and 3.88 nm, respectively, which are only slightly larger than that in fresh Pd/PANOF, Pd/LTCF-350 and Pd/LTCF-450 (Fig. 2). It should also be noted that an amount of Pd nanoparticles fell off the fibers indicating a possible mechanism for the deactivation of the catalyst due to the organic activating group.

In summary, we successfully designed a brand new catalytic system in which a palladium based catalyst can be directly attached on the inner wall of the reactor. It has indeed been demonstrated that the new system containing Pd/PANOF, Pd/LTCF-350 and Pd/LTCF-450 catalysts, together with the reactor was shown to be very highly active and selective for the Mizoroki–Heck cross-coupling with iodobenzene and acrylates. The high catalytic activities, easier separation and recycling make this unique environmentally benign heterogeneous palladium catalyst and the novel system attractive for large industrial-scale applications.

Experimental

Polyacrylonitrile (PAN, $M_w = 80\ 000$) was purchased from Kunshan Hongyu Plastics Co. Ltd. *N*,*N*-Dimethylformamide (DMF, C₃H₇NO, AR, 99.5%), palladium chloride (PdCl₂, AR), iodobenzene (C₆H₅I, CP, 97%), triethylamine (C₆H₁₅N, AR, 99%), methyl acrylate (C₄H₆O₂, CP, 98%), ethyl acrylate (C₅H₈O₂, CP, 98%), acrylonitrile (C₃H₃N, CP, 98%), acrylic acid (C₃H₄O₂, CP, 98%) and *n*-butyl acrylate (C₇H₁₂O₂, CP, 98%) were purchased from Sinopharm.

For the fabrication of the Pd/PANOF, Pd/LTCF-350 and Pd/ LTCF-450 catalysts, the homogeneous solution used for electrospinning was prepared by dissolving PAN in DMF at a concentration of 5 wt% by stirring for 12 h. Palladium chloride (PdCl₂) powder was mixed into a PAN-DMF blending solution in which the monomer of PAN and PdCl₂ was at a molar ratio of 50, and then intensively stirred for 24 hours. Fabrication of the PdCl₂-PAN nanofibers was typically achieved by electrospinning a blending solution containing PdCl₂-PAN-DMF, the blending solution was passed through a dropper with winding copper wire. The positive voltage applied to the winding copper wire was 16 kV and the distance between the winding copper wire and the collector was 12 cm. It is worth mentioning that the collector in this experiment was the reactor. In other words, the as-spun PAN-PdCl2 fibers were collected on the inner surface of the reactor. After that, 2 mol $L^{-1} N_2 H_4$ aqueous solutions were added into the reactor for 2 hours. After washing and drying in ambient air, the reactor was placed in a tube furnace and stabilized in air for 2 h at 250 °C to prepare the polyacrylonitrile preoxided fiber supported palladium catalyst (Pd/PANOF). Similarly, we successfully obtained the Pd/LTCF-350 and Pd/ LTCF-450 catalysts on the basis of stabilizing in air for 2 h at 250 °C and then heating up to 350 °C and 450 °C for 2 h in nitrogen.

In a typical procedure, a mixture of iodobenzene (1 mmol), acrylate (1.5 mmol), triethylamine (3 mmol) and DMF as a solvent (10 mL) were added into the reactor. After the reactor was screwed down, the reaction mixture was allowed to heat to 100 $^{\circ}$ C for 24 hours in a nitrogen atmosphere. After completion, the reactor mixture was cooled down to room temperature, the reactor was opened and the mixture was filtered. The products were examined by a 7890A gas chromatograph (GC) equipped with a FID detector, the chromatographic conditions were as follows according to different reaction substrates, the

temperature of the injection port and detector ranged from 220 to 280 °C. The temperature of the oven adopted temperature programming, the highest temperature ranged from 220 to 270 °C; chromatographic column was J&W 113-3032, SE-30. Sample volume was 0.3 μ L every time.

For the recycling experiments, after a catalytic run, the liquid phase was directly poured out from the reactor. Then, distilled DMF and water were added into the reactor to wash the catalyst. After being dried under vacuum, we directly reused the catalyst following the above described procedure.

Measurements

Pd/PANOF, Pd/LTCF-350 and Pd/LTCF-450 catalysts were investigated using a scanning electron microscope (SEM, S-3400, and Hitachi Ltd) and a transmission electron microscope (FEITEM, F20 S-TWIN, and Tecnai). The samples for TEM were dispersed in ethanol by an ultrasonic treatment, and then a drop of the dispersion was deposited on a TEM carbon-coated Cu grid and dried at room temperature. The X-ray source of the X-ray photoelectron spectroscopy (XPS, Escalab 250, Thermo-Fisher Scientific USA) was monochromatic Al K α at 150 W. Fourier Transform Infrared Spectroscopy (670, FTIR, Thermo Nicolet Corporation) was also performed. The UV-vis diffuse reflectance spectrum (DRS) (UV-3600, Shimadzu Corporation) was recorded to detect the presence of zerovalent palladium at a wavelength of 190 to 600 nm.

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