Fabrication and application of porous Pd@Mt/PC composite as an efficient green heterogeneous catalyst for Suzuki cross-coupling reaction

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The palladium-loaded montmorillonite (Pd@Mt) was mixed with polycarbonate (PC) solution to obtain Pd@Mt/PC composite. A different solvent was used to treat the Pd@Mt/PC coating so as to induce crystallisation of PC and fabricate a porous surface. The scanning electron microscopy and surface area measurement results proved this successful change. The Pd@Mt/PC that was treated by isopropanol fabricated a porous surface coating on glass microsphere (Pd@Mt/PC-M), which was found to be a conveniently obtained environment-friendly catalyst in the Suzuki reaction, as the Pd content was only 0.2012 ppm in the product solution. Notably, it exhibited high efficiency, affording the corresponding product in good to excellent yields for 20 reactants (in the range of 78–99%, only two reactants gained yield below 90%). As a heterogeneous catalyst, it could be easily recovered by simple filtration from the reaction mixture and a high yield of more than 90% at a third run was remained.

1. Introduction: The soluble noble metals coupled with certain ligands are widely used as efficient catalysts in the formation of the C–C bond, owning to their special electronic arrangements [1]. They play a more and more important role in many organic synthesis reactions, i.e. the synthesis of pharmaceuticals, agrochemicals and advanced functional materials. Yet the homogeneous catalyst frequently suffers from leaving residual noble metal embedded in the products, which may not only have a dramatic and deleterious effect on toxicity, conductivity or other properties of products, but also increase the expense of catalyst because of the loss of expensive noble metal. Hence, many efforts have been dedicated to environmentally friendly heterogeneous catalytic systems as alternative methods to overcome these problems, hoping it could greatly improve the separation procedure and reduce the cost of the catalyst [2, 3]. Recently, many kinds of materials such as alumina, silicas, zeolites, metal–oxide nanoparticles (NPs), ionic liquids and polymers have been developed as the support of noble metal NPs [4–15], wishing the NPs of noble metal can be bound strongly on the surface of supports to achieve remarkably high efficiency and reused conveniently without much loss of noble metals even under sonication or extensive stirring. Some porous support can help a lot to achieve high catalyst activity, because their surface is combined with pores in either microscale or mesoscale, the metal NPs can be dispersed in micropores and prevented from agglomeration, at the same time, the mesopores provided a good diffusion way of the reactant during the reaction [16, 17]. The porous polymer Metal–organic framework (MOF) synthesised by Yuan *et al.* [18] has a surface area as high as 4000 m²/g, the yield can be achieved 95–97% when palladium (Pd) was supported as a catalyst for Suzuki reaction. The novel organic polymer microspheres are thought to be an ideal candidate to stabilise noble metal NPs for catalyst, because it can be separated easily by sediment, centrifugation or filtration; and the microspheres with small particle size and large specific surface area (SSA) allowed the reactant to access the noble metal NPs easily, which may greatly accelerate the chemical reaction [19]. Zhang *et al.* [20] used specially prepared poly(*N*-isopropylacrylamide-acrylic acid-2-hydroxyethyl acrylate) micro gel particles as a specific template to support different noble metal NPs, deeming that they were a very promising catalyst.

However, most of the polymer microsphere supports suffer from limited substrates, exorbitant chemical modifiers or vacuum apparatuses, harsh preparation requirements and complex fabrication steps. Wang *et al.* [21] took 2 days to prepare cellulose-supported triphenylphosphine under nitrogen at 80°C, and spent another 20 h to load Pd under a nitrogen atmosphere to obtain the catalyst. The same difficulty was met when preparing the porous polymer Pd support MPTA-1. It needs to be synthesised using triallylamine in a situ polymerisation, which has to be completed in a complicated anionic/non-ionic or anionic surfactant system through organic–organic self-assembly procedure [22, 23]. To overcome these problems, Pd-loaded montmorillonite (Pd@Mt) was added to obtain Pd@Mt/polycarbonate (Pd@Mt/PC) composite coated on cover glass or glass microsphere and dipped into 1,4-dimethylbenzene or isopropanol. As soon as the non-solution-induced crystallisation of PC took place, a porous surface with various nanostructures was formed. The whole process was completed in a rather short time. The surface of porous Pd@Mt/PC coatings was detected comparably with a scanning electron microscope (SEM) and SSA measurement. The residue of Pd in the product solution, catalytic activity and reusability of catalyst were also deeply probed.

2. Experimental results
2.1. Materials: Na⁺-Mt (Mt, K10, surface area = 240 m²/g) was bought from Alladin Company. PC (PC, MI = 1 g/min, density = 1200 kg/m³) was provided by Bayer Co. Pd chloride was purchased from Aldrich Chemical. The cover glass (20 × 20 mm²), glass microsphere (30 mushes), solvents and other chemical reagents (analytical reagent (AR) grade) were bought from commercial resources.

2.2. Preparation of porous Pd@Mt/PC catalyst: Pd@Mt was obtained via the method shown in our previous paper [24]. About 1 g PC and 0.5 g Pd@Mt were mixed in 100 ml dichloromethane (DCM), then cover glasses or glass microspheres were permeated in the solution for 5 min, and taken out to evaporate DCM at room temperature. The cover glass and glass microsphere supported Pd@Mt/PC samples were named as Pd@Mt/PC-G and Pd@Mt/PC-M, respectively. The raw Pd@Mt/PC-G and Pd@Mt/PC-M were dipped into 1,4-dimethylbenzene and isopropanol

separately for 30 s. When 1,4-dimethylbenzene or isopropanol evaporated completely, the porous surface was formed and the catalyst was obtained.

2.3. Measurements and characterisations

2.3.1. Scanning EM: Tiny gold particles with a diameter of 2–3 nm were sprayed on the samples to make it conductive, then the surfaces morphologies were investigated with a Quanta 400F SEM (Oxford Instruments) at an acceleration voltage of 20 kV.

2.3.2. Surface area measurements: A V-Sorb 2800P micromeritics equipment (Beijing Jinai Tec. Com.) was used to manage SSA measurements. The sample's surface area was measured from the isotherms of N_2 via Brunauer–Emmet–Teller equation. The sample's median pore diameter was determined with the Barret–Joyner–Halenda method.

2.3.3. Thermogravimetry: Thermogravimetry (TG) data of Pd-Mt/PC-M was taken on an STA 449 F3 TG instrument (Netzsch Instrument Co.) by heating the samples with 10°C/min heating rate from 30 to 700°C at nitrogen atmosphere.

2.3.4. Catalytic activity: Aryl halides (1 mmol), phenylboronic acid (1.2 mmol), Pd@Mt/PC-M (15 mg), deionised water 10 ml, ethanol (EtOH) 10 ml and potassium carbonate (K_2CO_3) (2 mmol) were heated to 60°C, stirred continuously for 3 h. The mixture was extracted carefully with ethyl acetate and dried over anhydrous sodium sulphate (Na_2SO_4) afterwards. The product was characterised by ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR data. The conversion rate of every reaction was analysed by gas chromatography (GC).

2.3.5. Pd content of the product: The mixture of a typical Suzuki reaction was diluted with 20 ml ethyl acetate and dried over anhydrous Na_2SO_4 when the reaction was completed. The solution was subjected to an ICP-MS 7700 (Agilent, USA) via the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to determine Pd content.

2.3.6. Differential scanning calorimetry (DSC) measurement: About 3 mg of the coatings were carefully stripped and set in an aluminium pan to do the DSC measurement on a Q20 DSC instrument (TA Instrument Com.). The sample was heated at 180°C at a rapid heating rate of 20°C/min to destroy thermal history. After it was cooled to 60°C, the sample was heated to 200°C at the heating rate of 10°C/min.

3. Results and discussion

3.1. Surfaces morphology: According to Table 1, both Pd@Mt/PC-G and Pd@Mt/PC-M exhibited larger SSA, bigger pore width and wider pore width dispersion after the non-solvent treatment. A surface like that would be very suitable for the catalyst, as it can make more catalytic activity sites exposed and effectively increase the contact area of the catalyst. The porous surface can be seen intuitively in Fig. 1.

Table 1 SSA test results

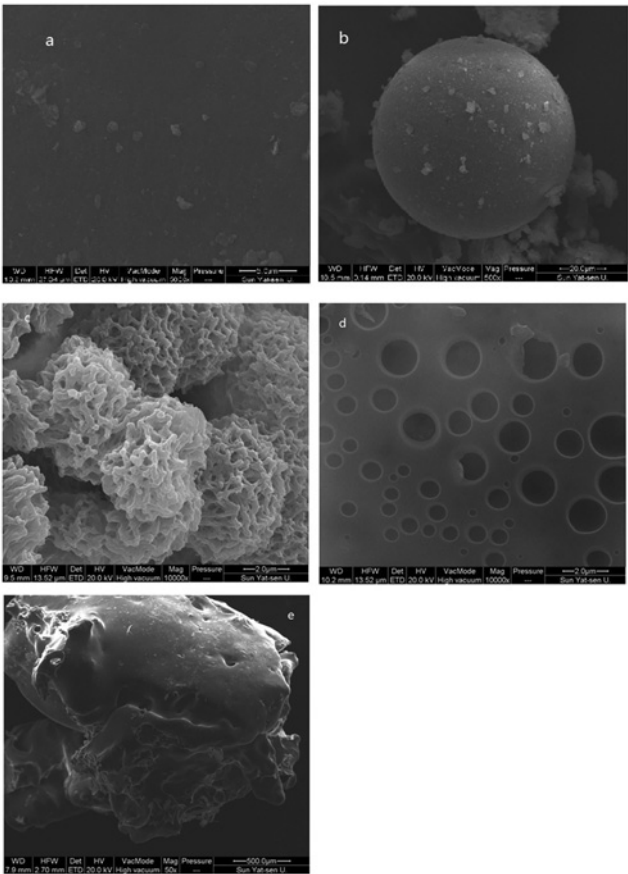| Sample	SSA, m^2/g	Pore width dispersion, nm	Barrett, Joyner and Halenda (BJH) median pore width, nm
untreated Pd@Mt/PC-M	15.03	2.25–346.79	3.15
untreated Pd@Mt/PC-G	11.49	2.09–242.71	2.09
Pd@Mt/PC-M	21.86	2.04–401.24	3.51
Pd@Mt/PC-G	17.19	2.04–276.03	2.52

Fig. 1 *SEM photographs of Pd@Mt/PC-G and Pd@Mt/PC-M*
a Untreated Pd@Mt/PC-G
b Untreated Pd@Mt/PC-M
c Pd@Mt/PC-G treated by 1,4-dimethylbenzene
d Pd@Mt/PC-M treated by isopropanol
e Pd@Mt/PC-M treated by 1,4-dimethylbenzene

To reduce the mass and volume of catalyst used in the reaction, high content of Pd@Mt was added when preparing Pd@Mt/PC. Therefore, it was easy to understand the surface of untreated Pd@Mt/PC-G and Pd@Mt/PC-M exhibited in the SEM photograph (Figs. 1a and b) was not uniform. However, it can be generally described flat. Both Pd@Mt/PC-G and Pd@Mt/PC-M presented another different scene after non-solvent treatment. As shown in Fig. 1c, the surface treated with 1,4-dimethylbenzene was markedly rougher, as many crystal spherulites and pores appeared. There were also big holes, but the diameter was not larger than 2 μm. The non-solvents can bring about remarkable enhancement in the mobility of molecular chain and a relevant decrease in glass transition temperature (T_g), which induced quick crystallisation; therefore, the fast precipitation of large molecular may be proposed to generate tiny nuclei [25]. The polymer-rich phase would group into cluster about the previously formed nuclei and expand in all directions. Ultimately, it developed further into all kinds of morphological structures [26]. However, when isopropanol was used, only pores with different sizes were formed (Fig. 1d). It may be contributed to the little solvency of PC which made isopropanol only infiltrate into the external surface of the PC coating and hardly induce much crystal. To confirm this, DSC was carried out and the result was shown in Fig. 2.

The T_g of untreated Pd@Mt/PC was 149.15°C, and the T_g of Pd@Mt/PC increased slightly to 152.65°C after isopropanol treatment, which proved the weak induce crystal ability of isopropanol. However, Pd@Mt/PC treated by 1,4-dimethylbenzene presented an obvious increase, the T_g was as high as 182.15°C, indicating the formation of a massive crystal.
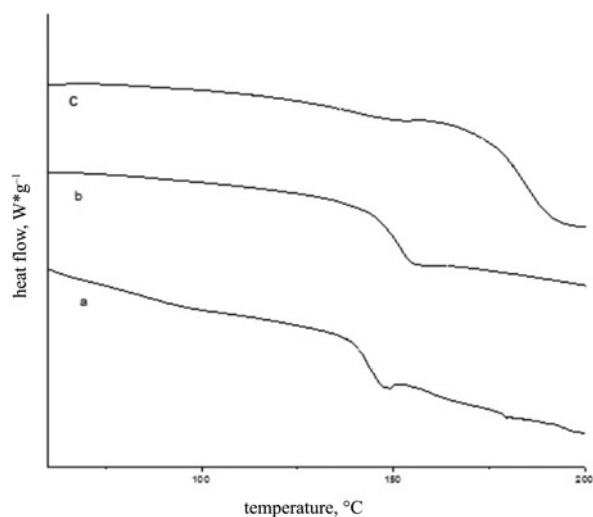
Fig. 2 *DSC curves of Pd@Mt/PC*
a Untreated
b Treated with isopropanol
c Treated by 1,4-dimethylbenzene

Although 1,4-dimethylbenzene can dilate and crack into the PC skin, exhibit high efficiency to induce crystallisation of PC, owning to the low compatibility for PC solution, high PC swelling ability and boiling points, it was not helpful to obtain microsphere with a porous tough Pd@Mt/PC surface, as serious adhesion occurred while it was used to treat Pd@Mt/PC-M, even when the treating time was cut to seconds (Fig. 1*e*). Turska and Janeczek demonstrated the process proceeded very quickly [27]. The lower boiling point of isopropanol (82.4°C) compared with 1,4-dimethylbenzene (138.3°C) made it evaporate much faster [28], which remarkably decreased the solidification time. The low solvency of isopropanol avoided penetrating into the coating and agglomeration of microspheres.

3.2. Catalytic activity and reusability: To accurately confirm the mass ratio of Pd@Mt attached, the glass microspheres were carefully weighted and coated with Pd@Mt/PC before managed on a TG instrument. The resident weight consisting of Pd@Mt and glass microsphere was 46 wt%, hence the mass ratio of Pd@Mt attached can be calculated as 27 wt%. Different mass of Pd@Mt/PC was added in 4-bromobenzaldehyde and phenylboronic acid to catalyse the typical Suzuki coupling reaction so as to appraise the catalytic efficiency. The catalytic efficiency gradually increased with the increasing catalyst content; the yields were 52, 92 and 99% when the Pd@Mt/PC-M content was 5, 10 and 15 mg, respectively. However, when the content of Pd@Mt/PC-M was even higher, the sustained increase of catalyst did not lead to further significant improvement of yields, which may be attributed to the nearly quantitative consumption of the starting material. From the above data, 15 mg Pd@Mt/PC-M that meant 4 mg Pd@Mt was sufficient to catalyse the reaction, which presented great progress comparing with our previous work on Pd@Mt as the catalyst of Suzuki coupling reaction (the Pd@Mt content used in the reaction was 20 mg). The turn over frequency (TOF) value was measured at low conversion rate (15%), the data showed that TOF of Pd@Mt/PC-M and Pd@Mt was 0.24 and 0.05 S^{-1}, respectively, which proved high activity of Pd@Mt/PC-M from the other side.

It was believed that the abundant porous structure can show a strong enrichment effect on the reactants, which helped to obtain a higher concentration of reactants in the catalyst channel and consequent better catalytic activity [29]. Besides, the holes with various diameters determined via SSA results and SEM photographs can play different roles in catalysis: Pd@Mt can be highly dispersed
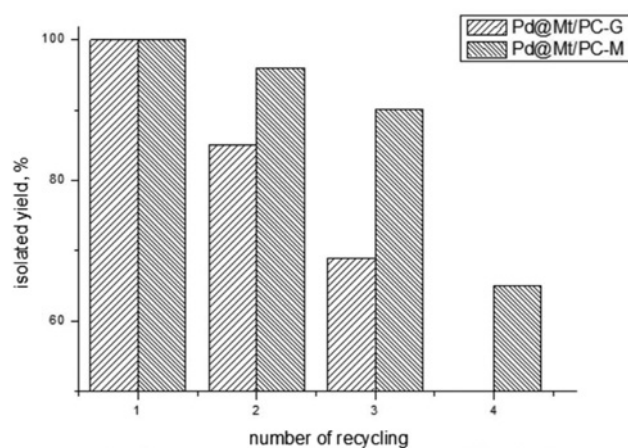

Fig. 3 *Reusability of Pd@Mt/PC-G and Pd@Mt/PC-M*

within micropores, preventing agglomeration of Pd nanoparticles (NPs) during the reaction, big hole and mesopores provided smooth channels for the internal diffusion of reactant. All of the advantages were helpful to improve the catalyst's activity. According to the previous ICP-AES results [24], the molar ratio between Pd and reactant was 1:4762, which was much lower than the previous report (0.012 mol% Pd): 1 mmol 4-iodoanisole) [30] and infected excellent catalytic activity.

To investigate the reusability of Pd@Mt/PC, 4-bromobenzaldehyde and phenylboronic acid were used as model reactants. The Pd@Mt/PC-G came off significantly on the cover glass after the second run. Meanwhile, the Pd@Mt/PC-M exhibited better reusability, the yields remained 90% in the third run (Fig. 3). The ICP-AES data showed that the content of Pd in Pd@Mt/PC-M was decreased from 0.15 (fresh one) to 0.09 wt% (after the third run), which explained its reusability. The difference of reusability between Pd@Mt/PC-G and Pd@Mt/PC-M may be that the coating did not completely cover the sharp edge of the cover glass, which resulted in swift abscission. By contrast, the microspheres were easy to roll and coated evenly, the coating was free from defects and better reusability was obtained. We once synthesise Pd@Mt/PC microsphere via emulsion. However, demulsification occurred occasionally and the microspheres obtained were too small to be filtered. On the whole, coating Pd@Mt/PC on glass microspheres was a most convenient way to obtain an efficient reusable supported Pd catalyst.

To explore the extensive catalytic activity of Pd@Mt/PC-M, multiple reactants were tolerated for the reactions under mild conditions. As shown in Fig. 4, the yields were almost all above 90% (with only the exception of two reactants), proving that Pd@Mt/PC-M was considerably effective for most of the substrates. It was believed that the appearance of both electron-donating and electron-withdrawing groups contributed to achieve the results [31]. The large porous surface area, which contributed a lot to the enrichment of the reactant around the Pd, was also thought to be helpful, as transmetalation from arylboronic acid to active centre was a fundamental process in Suzuki coupling. Generally, the conversion of LPd(Ar)(Br) (derived from the initial oxidation addition of the LPd(0) with ArBr) to LPd(Ar)–O–B–Ar' took place in the existence of arylboronic acid [Ar'B(OH)$_2$] [32]. This process was decelerated by ortho-substituted arylboronic acids, while can be boosted by the electron-donating groups. Accordingly, 4-methyl and 2,4-dimethyl into the arylboronic acid which showed no distinct influence on this transformation gave yields of 98 and 93%, respectively (entries 3 and 4, Fig. 4). When 2-methylphenylboronic acid was used as the substrate, the yields decreased slightly (entries 2, 7 and 12, Fig. 4). By contrast, the bulky 2-methoxylphenylboronic acid with electron-donating
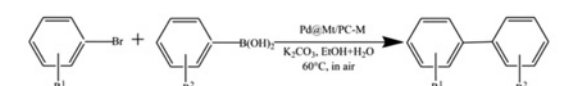
Entry	R^1	R^2	Yield (%) [b]
1	4-CHO	H	99
2	4-CHO	2-CH$_3$	93
3	4-CHO	4- CH$_3$	98
4	4-CHO	2,4-CH$_3$	93
5	4-CHO	2-OCH$_3$	99
6	4-COCH$_3$	H	99
7	4-COCH$_3$	2-CH$_3$	87
8	4-COCH$_3$	2,4-CH$_3$	97
9	4-COCH$_3$	2-OCH$_3$	99
10	4-COCH$_3$	4-OCH$_3$	99
11	4-Cl	H	99
12	4-Cl	2-CH$_3$	78
13	4-Cl	4- CH$_3$	95
14	4-Cl	2,4-CH$_3$	94
15	4-Cl	2-OCH$_3$	97
16	4-Cl	4-OCH$_3$	96
17	4-CN	H	95
18	4-CN	2-CH$_3$	94
19	4-NO$_2$	H	99
20	2-CN	H	94

[a]Reaction conditions: ArBr (1.0 mmol), ArB(OH)$_2$ (1.2 mmol), K$_2$CO$_3$ (2.0 mmol), EtOH:H$_2$O = 10 mL:10 mL, 3h, in air reaction condition. [b]Isolated yield.

Fig. 4 *Suzuki cross-coupling reactions catalysed by Pd@Mt/PC-M*

ability occurred at a yield of 97% (entry 5, Fig. 4). Therefore, it can be concluded that both the steric hindrance and the electronic-donating and -withdrawing ability of the arylboronic acid affected the efficiency of the coupling reaction. It can be seen in Fig. 4 that a series of aryl bromides accorded products with many arylboronic acids in exceptional yields (entries 6–19, Fig. 4). The aryl bromide reactants with ortho-substituent, which may decelerate oxidative addition and transmetalation during the catalytic cycle, was proved to be less active.

To analyse the catalytic mechanism, 4-bromobenzaldehyde and phenylboronic acid were selected as the coupling substrates and 300 equiv of Hg (0) was added. However, no product was observed under the standard reaction conditions. Besides, the reaction was quenched entirely when 100 equiv of other poisoning agents such as triphenylphosphine (P(C$_6$H$_5$)$_3$) were added. Obviously, these results suggested that a heterogeneous active species were involved in the reaction [33]. Then, a hot-filtration experiment was performed. First of all, a model reaction was carried out for 10 min and filtered while it was still hot. The yield of arylated product was confirmed to be 55% by GC analysis. The filter was maintained at 60°C and 2 equiv of K$_2$CO$_3$ was added. A 78% yield was obtained after further reaction for 150 min. It can be reasonably assumed that some amount of soluble Pd NPs were presented during the cross-coupling reactions. On the basis of researchers' reports [34, 35], there was a Pd(0)/Pd(II) pathway. In the first step, the Pd(II) complexes were reduced to Pd(0) species easily in the presence of arylboronic acid. Then, the oxidative addition of aryl bromide with Pd(0) species occurred, affording

the Ar–Pd(II)–Br intermediate. In the presence of a base, the intermediate subsequently undergoes transmetalation with arylbronoic acid to form the Ar–Pd(II)–Ar' intermediate. Finally, the catalytic cycle was completed via reductive elimination to produce the biaryl product and the active Pd(0) species was regenerated. According to our previous findings [24] and others' research [33, 36], there was evidence that heterogeneous active species were involved and soluble Pd NPs were presented during the cross-coupling reactions in the Pd@Mt catalysed reaction. As Pd was poisonous, it was important to reduce residual Pd embedded in products. To our delight, both Pd@Mt/PC-G and Pd@Mt/PC-M were environmentally friendly heterogeneous catalyst, the Pd content of product was remarkably low (0.2044 and 0.2012 ppm, determined by ICP test). In our previous research, the interaction between Pd and Mt helped to decrease the loss of Pd. In this case, the extremely small amounts of catalyst used in the reaction also contributed a lot to reduce the leaching of Pd.

4. Conclusion: Both 1,4-dimethylbenzene and isopropanol contributed to fabrication of suitable pores that were very helpful to disperse the catalytic active centre and diffuse reactant, resulting in enhanced activity of the catalyst. The Pd@Mt/PC-M was an excellent green catalyst for the Suzuki reaction, showing high efficiency within 20 reactants (with the molar ratio between Pd and reactant was 1:4762) and leaching remarkable tiny Pd content in the product solution (0.2012 ppm). It also exhibited good reusability, the yield was maintained more than 90% in the third run.

6 References

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