

Preparation of active and robust palladium nanoparticle catalysts stabilized by diamine-functionalized mesoporous polymers†

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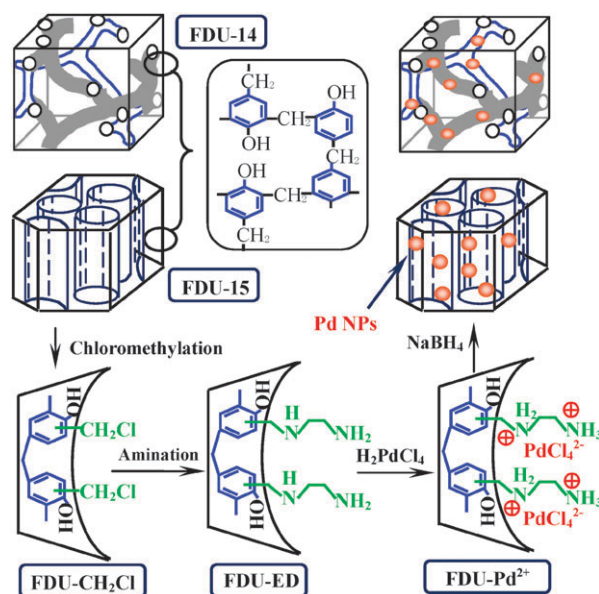
A two-step chemical modification process is designed for synthesizing novel diamine-functionalized mesopolymers, which combine the advantage of organic polymers and mesoporous materials, and serve as an efficient scaffold for supporting highly dispersed, catalytically active and robust Pd nanoparticles (NPs).

Ordered mesoporous materials have been extensively studied for their promising applications in separation, adsorption, catalysis, biological uses, and also as host–guest functional materials *etc.*¹ Among the mesoporous material family, the mesoporous phenolic resins (resols) are a class of advanced materials,² which possess the textural porosities of mesoporous materials (well-ordered pores, large surface area and tunable structures) and simultaneously the advantages of organic polymers (high hydrophobicity, containing aromatic sections and higher stability in acid or base media in comparison to silica-based materials). Recently, the use of polymers or mesoporous materials as the supports of metal nanoparticles (NPs) has attracted particular attention because of the unique physico-chemical characteristics and attractive catalytic performance of the resultant supported metals.^{3,4} For example, the reusable polymer-incarcerated (PI) Pd and Au NPs are reported to be stabilized by the benzene rings of the polystyrene moiety, which results in a highly active Pd catalyst for hydrogenation and Heck reaction,^{5a} and also an effective PI Au catalyst for the aerobic oxidation of alcohols.^{5b} On the other hand, the mesoporous materials have been widely used as ideal scaffolds for supporting Pd NP catalysts since their well-ordered mesostructures and regular nanopores may prevent the metal particles from agglomerating and also allow a ready diffusion of substrates to the catalytic sites.⁶ So more promising heterogeneous metal catalysts are thus expected to combine the advantages of the organic polymers and mesoporous materials.

In this sense, Fudan University (FDU)-type mesopolymers with a phenolic resin framework and tunable mesopores provide us with a good opportunity for designing such mesopolymer-supported metal catalysts.² The metal NPs would be highly dispersed inside the confined mesoporous, and further be stabilized by the π -electrons of benzene ring moieties of the mesopolymers, which may lead to an enhanced stability against deactivation.⁵ Nevertheless, it is still a great challenge

to search for a practicable chemical methodology suitable for dispersing uniformly the metal within the mesopolymers rather than through post-impregnation. Herein, we disclose a unique method for preparing the novel diamine-functionalized mesopolymers first, and then highly dispersed Pd NP catalysts with the assistance of these suitable polymer scaffolds. This new heterogeneous Pd catalyst proves to be a highly active, robust and durable heterogeneous catalyst in the reactions of C–C coupling and hydrogenation. This method could be used as a versatile way for preparing other mesopolymer-supported nanosized metal catalysts.

Scheme 1 shows the strategy for preparing the novel diamine-functionalized mesopolymers as the supports of Pd NPs. The chloromethylated materials, FDU-CH₂Cl, were first prepared through anchoring the CH₂Cl groups to the benzene rings of the mesopolymers. A subsequent functionalization of FDU-CH₂Cl in ethylenediamine (ED) solution affords diamine-modified materials, FDU-ED. When FDU-ED was subsequently stirred and formed a homogeneous suspension in the H₂PdCl₄ solution (containing 6 wt% Pd loading), the Pd(II) ions were complexed rapidly with the diamino groups through protonation and ionic interaction to lead to a colorless filtrate (Fig. S1†). Inductively coupled plasma (ICP) analysis indicated that the amount of Pd remaining in the filtrate was 0.95 ppm, which means that >99% of added Pd(II) was sucked into the polymers. After reduction in NaBH₄ solution, the Pd species



Scheme 1 Strategy for preparation of the mesopolymer-supported Pd NPs.

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formed the NPs dispersed and immobilized inside the mesopores to obtain FDU-Pd. In contrast, unfunctionalized FDU mesopolymer with a high hydrophobicity not only showed a poor wettability in the H_2PdCl_4 solution but was virtually ineffective for capturing the Pd(II) ions (Fig. S1†).

The modification processes were monitored and confirmed with FTIR and elemental analyses. FDU- CH_2Cl contained 1.9–2.2 mmol g^{-1} chlorine and showed a new band at 695 cm^{-1} assigned to the stretching vibration of the C–Cl bond (Fig. 1). This band disappeared upon the diamine treatment while three additional bands were developed distinctly at 3360, 1645 and 1020 cm^{-1} attributed to the N–H stretching, N–H bending and C–N bending vibrations, respectively. The N content of FDU-ED was 3.6–4.0 mmol g^{-1} , which was almost twice the Cl content in the CH_2Cl groups. These results indicate that the diamine reacted almost stoichiometrically with the CH_2Cl groups to form the C–N bonds covalently attached to the mesopolymer walls.

Mesostructures were well preserved after stepwise chemical functionalizations and Pd loading, because the materials showed in the low-angle XRD patterns well resolved [211], [220], [420], and [332] planes due to a three-dimensional (3D) bicontinuous cubic structure (*Ia3d*) for the FDU-14 samples, as well as defined [10], [11] and [20] planes of a 2D hexagonal structure (*P6mm*) for the FDU-15 samples (Fig. 2). However, the FDU-Pd materials showed no characteristic diffraction of Pd in the wide-angle region, implying that the Pd particles were smaller than the detection limit of XRD.

The HRTEM image of FDU-14-Pd viewed along the [311] direction verified together with the selected area electron diffraction pattern (inset) that the ordered cubic mesostructure (*Ia3d*) remained intact after immobilizing the Pd NPs (dark spots) (Fig. 3A). The Pd particles appeared to be dispersed mainly inside the mesopores, having a uniform size (average diameter of 1.8 ± 0.5 nm). Only a few particles with a slightly larger size (3–3.5 nm) were formed, probably as a result of the agglomeration of Pd(II) ions nearby the pore entrance in the reduction process. On the other hand, FDU-15-Pd contained the Pd particles with an average diameter of 2.0 ± 0.3 nm dispersed predominantly inside well-ordered hexagonal channels (Fig. 3B). Thus, with the assistance of the diamino groups, Pd NPs with a narrow size distribution and a high dispersion were confined successfully inside the channels of the mesopolymers.

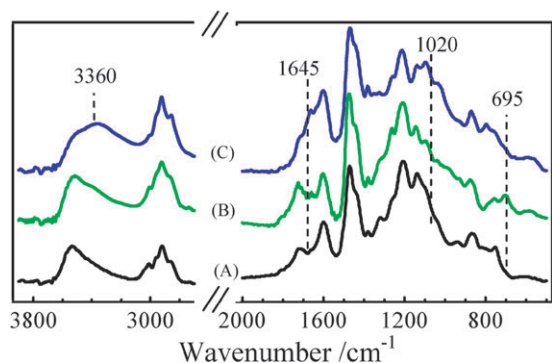


Fig. 1 FTIR spectra of (A) FDU-14, (B) FDU-14- CH_2Cl , (C) FDU-14-ED.

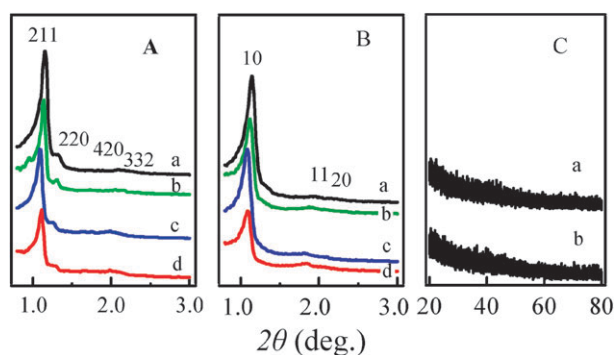


Fig. 2 Low-angle XRD patterns of (A) (a) FDU-14, (b) FDU-14- CH_2Cl , (c) FDU-14-ED, (d) FDU-14-Pd; (B) (a) FDU-15, (b) FDU-15- CH_2Cl , (c) FDU-15-ED, (d) FDU-15-Pd; and wide-angle XRD patterns of (C) (a) FDU-14-Pd, (b) FDU-15-Pd.

Using FDU-15-Pd as a representative, we have investigated the catalytic activity of the mesopolymer-supported Pd NPs in the Heck and hydrogenation reactions. The FDU-15-Pd catalyst was air-stable and recoverable when it catalyzed the C–C coupling of aryl halides with ethyl acrylate in air (Table 1). With a low Pd content (0.028 mol%), the Heck reaction of iodobenzene took place readily at temperatures ranging from 50 to 130 °C (entries 1–5). It is noteworthy that a conversion high as 93% was achieved at 50 °C after a prolonged reaction

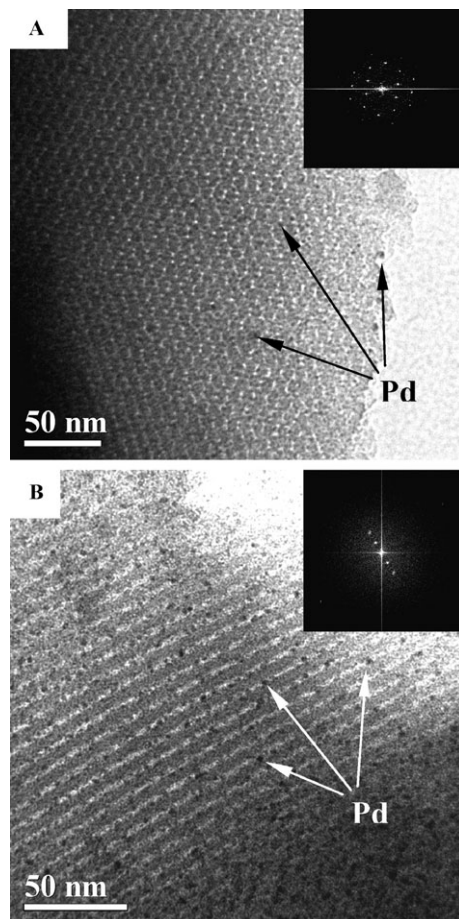
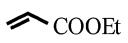



Fig. 3 HRTEM images of (A) FDU-14-Pd viewed in the [311] direction, (B) FDU-15-Pd viewed in the [10] direction.

Table 1 Catalytic results of Heck reactions^a

Ar-X + 		FDU-Pd in DMF		Ar- 		
Entry	Cat.	Substrate	Temp./ °C	Time/h	Conv. (%)	TOF/h ⁻¹
1	FDU-Pd	PhI	50	86.00	93	39
2	FDU-Pd	PhI	80	6.00	99	590
3	FDU-Pd	PhI	110	1.00	96	3429
4	FDU-Pd	PhI	130	0.25	92	13 054
5	FDU-Pd	PhI	130	0.33	100	10 642
6	Sixth reuse	PhI	130	0.25	91	—
7	FDU-Pd ^b	PhI	130	0.25	91	—
8	FDU-Pd ^{2+c}	PhI	130	1.00	Trace	—
9	FDU-Pd	2-MeO-PhI	130	0.67	98	5250
10	FDU-Pd	3-MeO-PhI	130	0.50	99	7072
11	FDU-Pd	4-MeO-PhI	130	0.33	95	10 179
12	FDU-Pd	2-CF ₃ -PhI	130	2.50	96	1372
13	FDU-Pd	3-CF ₃ -PhI	130	0.67	95	5090
14	FDU-Pd ^d	4-NO ₂ -PhBr	130	4.20	96	82
15	FDU-Pd ^e	PhBr	140	50.00	72	3



^a Pd = 0.028 mol%, ArX = 10 mmol, ethyl acrylate = 12 mmol, NEt₃ = 12 mmol, DMF = 10 mL. ^b After being stored in air for one month. ^c Not reduced. ^d Pd = 0.28 mol%. ^e Pd = 0.6 mol%, K₂CO₃ = 12 mmol.

time. With the reaction temperature increasing to 130 °C, the TOF of FDU-Pd reached as high as 10 642 h⁻¹, a superior activity to other reported Pd-based heterogeneous catalysts.^{5a,7} To gauge the catalytic generality of FDU-Pd, it was further applied to the Heck reactions of a range of aryl halides with electron-donating or -withdrawing substituents. It showed an excellent conversion (>95%) for various substrates and was capable of giving 72% conversion for inactive bromobenzene (entries 9–15). In a control experiment, unreduced FDU-Pd²⁺ yield only a trace amount of product even after a prolonged reaction (entry 8). This means the Pd(0) NPs served as the true active species for Heck reaction.

After the workup, the amount of Pd leached into the reaction mixture was below the detection limit of ICP, and a hot leaching test clearly showed that the reaction stopped when the filtrate was further subjected to the same reaction (Fig. S5†). After being recycled for six runs, the Pd catalyst showed a remarkable conversion (91%) (Table 1, entry 6), and remained inside the mesopolymer pores as evidenced by HRTEM (Fig. S6†). Moreover, FDU-Pd was comparably active after being stored in air for one month (entry 7). This feature is obviously different from air- and moisture-sensitive homogeneous Pd stabilized with the phosphine ligands, also different from other heterogeneous Pd catalysts such as Pd/SiO₂, Pd/Al₂O₃, Pd/C and Pd/SBA-15 which are reported to suffer the Pd leaching to a certain extent in the Heck reaction.^{6a,8} All these results consistently suggest that FDU-Pd has the advantages of good reusability and high catalytic activity. This could be attributed to the confining effect of mesopores as well as the stabilizing ability of benzene rings for metal NPs, which prevent the Pd NPs from aggregating into less active Pd black and from leaching as well.

Under mild conditions, FDU-Pd catalyzed actively the hydrogenation of allyl alcohol to produce 1-propanol (Table 2). In comparison to a commercial 5 wt% Pd/C catalyst which is

Table 2 Catalytic results of allyl alcohol hydrogenation reaction^a

Cat.	Substrate	Conv. (%)	Selectivity (%)	TOF/h ⁻¹
FDU-Pd		100	83 ^b	2944
5wt% Pd/C	 + H ₂	95	74 ^b	2138

^a Pd = 0.056 mol%, allyl alcohol = 10 mmol, H₂ = 1 atm, 30 °C, 30 min. ^b Byproduct was acetone.

extensively used in industry, the FDU-Pd catalyst showed a significantly higher TOF, allyl alcohol conversion as well as 1-propanol selectivity. In addition, in the kinetic and recycling experiments, FDU-Pd was confirmed to show a high stability and reusability for the hydrogenation (Fig. S7 and S8†).

In summary, we have developed diamine-functionalized mesopolymers which serve as promising scaffolds for dispersing and stabilizing Pd NPs. The FDU-Pd catalysts were air-stable, durable, highly active and reusable in C–C formation and hydrogenation reactions without leaching of Pd species. The method explored here can be used as a valid way for designing and preparing Au, Pt, Ru and Rh nanoparticle catalysts.

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