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Aminated chlorinated polyvinylchloride nanofiber mat-supported palladium heterogeneous catalysts: preparation, characterization and applications†

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Chlorinated polyvinylchloride (CPVC) nanofiber mats were prepared by an electrospinning technique, and then treated with amines of different chemical structures, followed by immobilization of palladium catalysts (CPVC–NH_2–Pd), which have been demonstrated as efficient, stable and easily recyclable heterogeneous catalysts. Their catalytic activities could be correlated with the binding energies of the palladium species with the amine chelating ligands.

Catalysis plays a significant role in synthetic organic chemistry as it can greatly facilitate chemical transformations.[1] Heterogeneous catalysis has received tremendous interest because catalyst reuse and recycling can further improve the overall productivity and cost-effectiveness, thereby minimizing the waste generation and catalyst contamination, leading to a greener and more sustainable chemical transformation process.[2–4] However, there are still many challenges for preparing efficient, stable and easily recyclable palladium heterogeneous catalysts. First, the zero-valent palladium species generated from the catalytic cycle is prone to aggregate and then lose the catalytic activity by formation of palladium black. Second, heterogenization reduces the accessibility and in turn decreases the catalytic activity because the reactants can only access the surface-bound catalytic centers, rather than all accessible in a homogeneous system.[2–4] Finally, the solid supported matrices are generally fabricated in small fine particles to maximize the surface area to mass ratio, evolving into a tedious and time-consuming process by separation and recycling of the particulate catalysts from the reaction mixture due to the high pressure drop by filtration, especially in the large-scale industrial applications.[5]

Nanofiber mats have been used as the supporting matrixes for immobilizing palladium and other transition metal catalysts because of their high specific surface area, allowing high dispersion of the catalytic active species.[6] In addition, the characteristic intact structure of the nanofiber mat allows much easier removal of the heterogeneous catalysts from the reaction mixture by simple filtration. However, the reported nanofiber mats-supported palladium heterogeneous catalysts usually suffer relatively low stability, mainly due to the relatively weak absorption of the palladium species onto the nanofiber mats.[7–9] We hypothesized that introduction of strong chelating ligands onto the surface of the highly porous nanofiber mats should increase chelation of the palladium species with the surface molecules of the supporting matrixes, which might improve the catalytic activities and stabilities while retaining the large intact nanofiber mat structure. Unfortunately, most of the strong chelating ligands cannot survive the oxidative degradation at the high temperature and electric voltage required by the electrospinning protocol. Our strategy was inspired by the easy amination of polyvinylchloride with amines under mild reaction conditions.[10,11] Thus we have prepared the nanofiber mat using chlorinated polyvinylchloride (CPVC), then modified the surface with different amines, followed by immobilization of the palladium catalyst (CPVC–NH_2–Pd) as depicted in Fig. 1. Herein, we describe the use of this approach to construct a series of CPVC–NH_2 nanofiber mat-supported palladium heterogeneous catalysts, which have been demonstrated as highly efficient, stable and recyclable heterogeneous catalysts for the Heck cross-coupling reactions.

CPVC was shown as an excellent polymeric material for preparing the nanofiber mats by means of electrospinning technique. The CPVC concentration and feeding rate might be used up to 20 wt% and 2.5 ml h^{-1}, respectively. However, the resultant CPVC nanofiber mats were soluble in the polar organic solvents such as DMSO, DMF, chloroform, *etc.*, limiting their applications in the organic solutions. No improvement for the solvent resistance was achieved when the CPVC nanofiber mats were treated with mono amines such as *n*-propyl amine

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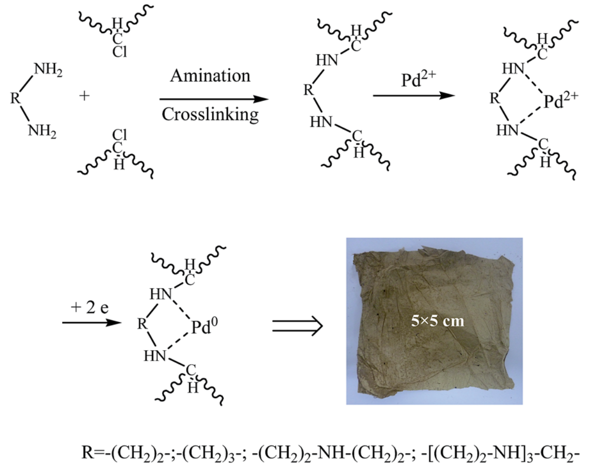

Fig. 1 Schematic illustration for the preparation of the aminated CPVC nanofiber mat-supported palladium catalysts.

using the literature procedure reported for the amination of polyvinylchloride.[11] Most intriguingly, a significant improvement of resistance was obtained to the polar organic solvents when the CPVC nanofiber mats were treated with bidentate amines such as 1,3-propylenediamine, termed as CPVC–NH_2 nanofiber mats. For example, no much morphological variation was observed for the CPVC–NH_2 nanofiber mats even after soaked in DMF solution for 36 hours (also see Fig. 2c). Moreover, the mechanical tensile strength was found to increase significantly from 6.50 ± 1.34 MPa (CPVC nanofiber mat) to 11.08 ± 1.56 MPa (CPVC–NH_2 nanofiber mat) when treated with 1,3-propylenediamine. The significant tensile strength increase from the treatment of bidentate amines signified a cross-linking structure of the CPVC–NH_2 nanofiber mats. The CPVC and CPVC–NH_2 nanofiber mats were deposited with the palladium catalyst according to the similar procedure as reported previously.[5] Although negligible palladium species was immobilized on the untreated CPVC nanofiber mats, the palladium content of the CPVC–NH_2–Pd heterogeneous catalyst was determined to be about 3.0 wt% based on the ICP-AES analysis.

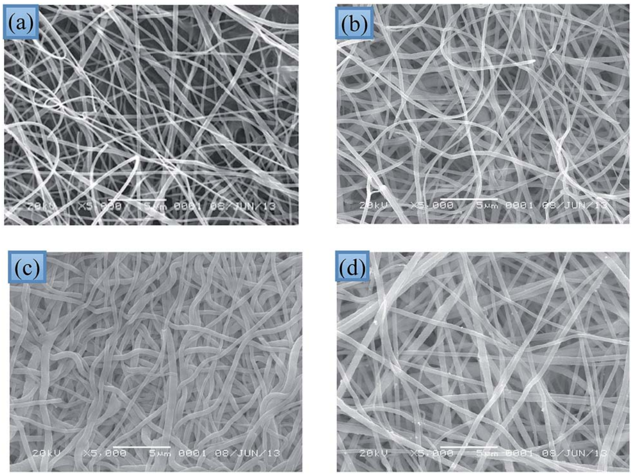

Fig. 2 SEM images: (a) CPVC nanofiber mat, (b) CPVC–NH_2 nanofiber mat aminated by 1,3-propanediamine, (c) aminated CPVC nanofiber mat after soaked in DMF for 36 hours and (d) CPVC–NH_2–Pd catalyst.

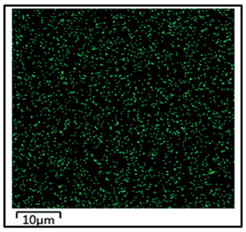

Fig. 3 SEM-EDS image for the CPVC–NH_2–Pd catalyst.

Examination of the IR spectra (Fig. 1S of the ESI†) shows that there are two broad characteristic IR absorptions at 1630 and 3418 cm^{-1}, which can be attributed to the >NH functional group of the CPVC–NH_2 nanofiber mats. The slightly blue shifts of the amine IR absorption bands after immobilization of the palladium catalyst can be attributed to the chelation of the amine groups with the palladium species. Nevertheless, the elemental analysis showed that the resultant CPVC–NH_2 nanofiber mat contained 1.16 ± 0.06% weight of nitrogen, *i.e.* 0.08 mol per 100 g of the amine functional group content, providing the conclusive evidence for the amination.

The morphological features of the prepared nanofiber mats have been examined by means of the scanning electron microscopic (SEM) technique. The essentially identical SEM images of the CPVC nanofiber mats (Fig. 2a), CPVC–NH_2 nanofiber mats (Fig. 2b) and CPVC–NH_2–Pd nanofiber mats (Fig. 2d) suggested that the amination and palladium immobilization had negligible effects on the morphological structure of the nanofiber mats.

The palladium deposition of the CPVC–NH_2–Pd heterogeneous catalysts was further examined by the X-ray diffraction (XRD) and SEM-EDX analysis. The weak Pd(111) characteristic pattern (Fig. 2S†) was consistent with the amorphous structure of the immobilized palladium species on the CPVC–NH_2 nanofiber mats. The SEM-EDX image (Fig. 3) of the

Table 1 The catalytic activities and chelating energies of the aminated CPVC nanofiber mat supported palladium heterogeneous catalysts[a]

Amine ligands	Conversion (%)	Yield[b] (%)	ΔH^c (kJ mol^{-1})
1,3-Propanediamine	97 ± 3	93 ± 2	−34
Ethylenediamine	92 ± 3	88 ± 1	−93
Diethylenetriamine	89 ± 1	84 ± 1	−123
Tetraethylenepentamine	85 ± 1	84 ± 2	−206
Pd/C	90 ± 4	83 ± 3	—

[a] Reaction conditions: palladium catalyst: 50 mg; iodobenzene: 0.70 mmol; *n*-butyl acrylate: 1.4 mmol; DMSO: 3.0 ml; CH_3CO_2K: 5.25 mmol; reaction temp.: 110 °C; time: 1.0 hour. [b] Cross-coupling yields were determined from the GC/MS measurements based on the amount of aromatic halide substrate. Results were the average from three separate experiments. [c] Gaussian 03 calculation: B3LYP function with SDD//6-31G(d) basis set.

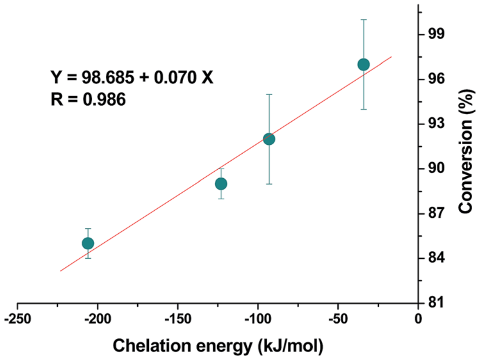

Fig. 4 Linear correlation of the catalytic activities with the chelation energies of the palladium species with the amine ligands (Table 1).

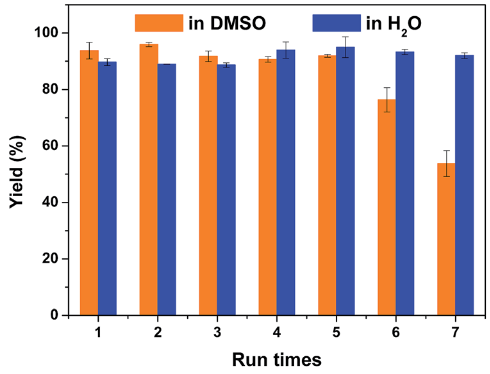

Fig. 5 Reuse of the CPVC–NH_2–Pd catalyst in both DMSO and aqueous solutions.

CPVC–NH_2–Pd heterogeneous catalyst clearly indicated that the immobilized palladium species was uniformly dispersed onto the surface of the nanofiber mats. The invisible palladium species from the SEM images (Fig. 2d) could be attributed to its relatively small size, which was estimated to be about 3.2 nm from the Scherrer equation.[12]

The palladium catalyzed Heck cross-coupling reactions have widely been used to construct the carbon–carbon bond transformations from two sp^2 hybridized carbons.[13–15] In this study, we employed the Heck cross-coupling reaction of aromatic iodides and acrylates as a model reaction to assess the catalytic activity, stability and recyclability of the prepared CPVC–NH_2–Pd heterogeneous catalysts in both DMSO and aqueous solutions. The initial reaction conditions were adapted from our previous studies,[7,8] which were optimized for the chitosan microsphere supported palladium catalyst. The conversion and cross-coupling yields were determined to assess the catalytic activities of the resultant CPVC–NH_2–Pd heterogeneous catalysts.

Examination of Table 1 shows that the catalytic activities of the CPVC–NH_2–Pd heterogeneous catalysts are considerably higher than that of the carbon supported palladium catalyst under the same conditions. Most interestingly, the activities of the prepared CPVC–NH_2–Pd catalysts were dependent upon the chemical structure of the multiamines although their morphological and mechanical features are essentially identical. Further-more, the catalytic activities could be linearly correlated with the chelating energies of these amine ligands with the palladium species as determined by a density functional theory calculation at the B3LYP/6-31G(d)-SDD level as summarized in Fig. 4. The linear correlation clearly suggests that the coordination with the stronger chelating ligand will result in more difficult reduction of the divalent palladium (Pd^{2+}) into the zero-valent palladium (Pd^0) species, leading to a lower catalytic activity.

Cross-coupling products were obtained in excellent yields from both organic and aqueous solutions (Fig. 5). There were negligible effects on the catalytic activity of the recovered CPVC–NH_2–pd catalyst from the aqueous solution reaction even after seven recycling times. But the catalytic activity was found to gradually decrease after five recycling times for the recovered CPVC–NH_2–Pd catalyst from the DMSO solution reaction as shown in Fig. 5. The relatively lower stability of the CPVC–NH_2–Pd catalyst in the DMSO solution is presumably associated with the stronger chelation of the palladium species with the solvent DMSO molecules relative to the water molecules. This conclusion is consistent with the DFT calculations, which clearly showed that the chelation energy of DMSO with Pd (ΔH: -224 kJ mol^{-1}; ΔG: -150 kJ mol^{-1}) was much larger than that of Pd with H_2O (ΔH: -137 kJ mol^{-1}; ΔG: -72 kJ mol^{-1}). Furthermore, the ICP-AES analysis showed that the palladium contents of the recovered CPVC–NH_2–Pd catalysts were 2.32 ± 0.11% and 2.43 ± 0.13% after five cycles from the DMSO and H_2O solutions, respectively.

Table 2 Heck cross-coupling reactions of various aromatic halides with different acrylates[a]

Entry	Aromatic iodides	Acrylates	Time (hours)	Yield[b] (%)
1	4-FC_6H_4I	$CH_2 = CHCO_2(n\text{-Bu})$	6	94/91
2	4-BrC_6H_4I	$CH_2 = CHCO_2(n\text{-Bu})$	6	92/90
3	4-ClC_6H_4I	$CH_2 = CHCO_2(n\text{-Bu})$	6	97/94
4	4-$CH_3C_6H_4I$	$CH_2 = CHCO_2(n\text{-Bu})$	8	94/88
5	4-$NO_2C_6H_4I$	$CH_2 = CHCO_2(n\text{-Bu})$	8	99/95
6	C_6H_5I	$CH_2 = CHCO_2(n\text{-Bu})$	3	90/84
7	C_6H_5I	$CH_2 = CHCO_2CH_3$	3	98/92

[a] Reaction condition: aromatic iodides: 0.70 mmol; acrylate: 1.4 mmol; DMSO: 3.0 ml; CH_3CO_2K: 5.25 mmol; reaction temperature: 110 °C. [b] Cross-coupling yields were determined from the GC/MS measurements/isolated yield based on the amount of aromatic halide substrate.

The prepared CPVC–NH_2–Pd catalysts were also applicable to the Heck reactions of other aromatic iodides and acrylates. Table 2 presents few representative results as catalyzed by the 1,3-propylenediamine modified CPVC nanofiber mat supported palladium catalyst. Clearly, the new palladium heterogeneous catalysts worked very well for the Heck cross-coupling of the aromatic iodides bearing either an electron donating or an electron accepting substituent.

In summary, CPVC nanofiber mat has been prepared by electrospinning. Amination of the CPVC nanofiber mats with multiamines could improve the chelating ability, solvent resistance and mechanical properties. The catalytic activities could be tuned by the chemical structures of the multiamines. The CPVC–NH_2-supported palladium has been demonstrated as an efficient, stable and easily recyclable heterogeneous catalyst for the Heck cross-coupling reactions in both organic and aqueous solutions.

Acknowledgements

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