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Received 00th January 20xx, Accepted 00th January 20xx DOI: 10.1039/x0xx00000x www.rsc.org/

Controlled synthesis of uniform palladium nanoparticles on novel micro-porous carbon as a recyclable heterogeneous catalyst for Heck reaction

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Novel dual-porous carbon-supported palladium nanoparticle (Pd NP) catalysts were prepared by sequential carbonization and reduction of microporous organic polymer-encaged PdCl₂. The diverse pore structure of microporous organic polymers provides a reservoir for the palladium precursors and prevents Pd NPs from sintering during the carbonization and reaction. The microporous structure has a significant effect on the size and dispersion of palladium NPs. The average size of the Pd NPs (in the range of 4-6 nm) was tuned by changing the pore size distribution and the carbonization temperature. The resulting carbon-supported Pd NPs were characterized by TEM, BET, XRD, XPS and the Pd loading was calculated by AAS. The encaged Pd NP catalysts prepared by this methodology exhibited outstanding stability and reusability in Heck reaction which could be reused at least 10 times without appreciable loss of activity.

Introduction

Palladium catalysts play an important role in organic syntheses, chemical and pharmaceutical process. Most applications in these processes involve homogeneous catalysts consisting of palladium complexes with a variety of ligands.¹ However, homogeneous catalysis has certain limitations including the separation, recovery and regeneration of the catalyst that are the key factors to make the processes costeffective. A series of attempts have been made to overcome these problems by using heterogeneous Palladium catalyst systems. Because the metal size and dispersion have an essential impact on the catalysts activity, many researchers have concentrate on the method of preparation high dispersed and excellent catalytic efficiency heterogeneous palladium catalysts.²

The palladium-catalysed Heck coupling reaction has

received increasing attention in the last decade due to the enormous synthetic potential to generate new carbon-carbon bonds.³ Recent studies are attempted to immobilize Palladium NPs on various supports such as carbon,⁴ magnetic materials,⁵ silica,⁶ hydroxyapatite,⁷ zeolites,⁸ MOFs⁹ and organic polymers¹⁰ to create heterogeneous catalysts system. Among these supports, activated carbons have been well addressed due to numerous promising applications in heterogeneous catalysis. Carbon has a highly disorganized structure of aromatic sheets and strips, high surface area and offers various active sites due to the presence of several functional groups within its pores.¹¹ The cost-effectiveness, easier availability, appropriate thermal and mechanical properties also make carbon based supports more attractive for heterogeneous catalysis. There are several reports to prepare carbon supported metal catalysts, including palladium, but they often suffer from substantial metal/Pd leaching (e.g. 14 % of Pd is leached from Pd/C)¹² and the aggregation of metal/Pd NPs at high temperature. So the major limitation of Pd/C catalysts, whether they are commercially available or generated in situ, is their poor recyclability.

Therefore, the synthesis of palladium nanoparticles (NPs) immobilized on porous supports has attracted extensive interest in heterogeneous catalysis.¹³ The catalytic activity of palladium NPs is known to depend on their size and degree of dispersion. Much effort has been devoted to embedding palladium NPs into porous materials containing coordination groups, which can offer potential for the control of particles size and prevention of NPs aggregation.¹⁴ So the controlled synthesis of catalytically active Pd NPs with stable and narrow

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⁺ Electronic Supplementary Information (ESI) available: Experimental details of the synthesis of C-(KTB-Pd), C-(KB-Pd), C-(CPR-Pd). XPS characterises, Pore size distribution and ¹H NMR data. See DOI: 10.1039/b00000x

DOI: 10.1039/C5DT02133B

Journal Name

Published on 19 June 2015. Downloaded by University of Queensland on 23/06/2015 17:11:27

size distribution has become the research focus of the leading researchers in catalysis. $^{15}\,$

We report the design and synthesis of a "dual-porous" carbon material with the possibility to replace conventionally used active carbons. Ordered mesoporous carbons (OMCs) are generally prepared with a hard-templating method relying on mesoporous silica,¹⁶ porous coordination polymers (PCPs) or metal-organic frameworks (MOFs), which are crystalline compounds consisting of metal ions coordinated to the rigid organic framework to form one-, two-, or three-dimensional structures.¹⁷ A new approach is also demonstrated to prepare novel microporous carbon materials by the carbonization of microporous organic polymers (MOPs) followed by the immobilisation of Pd NPs in pore structure, combining the advantages of MOPs with micro-sized supporting entities that resulted in a highly active and recoverable catalyst.¹⁸ Recently various strategies are being developed to produce diverse classes of porous carbon materials. Among these porous materials, MOPs with extraordinary high surface area have attracted extensive attention due to their unique properties such as large surface area, low skeletal density, and high chemical stability. One particular advantage of MOPs is to allow the fine dispersion and stabilization of small metallic particles. There are, however, only a few reports on MOPs supported metal nanoparticles with tunable metal NPs size distribution, especially during the process of carbonization. Compared to other porous materials, MOPs have the narrow pore size distribution and complicated pore structures, which prevents the metal particles sintering during the hightemperature annealing.

It has been observed that the leached palladium species from the supported catalysts are the real active species in the Heck reaction, which can be re-deposited onto the surface of the support when the aryl halides are depleted.¹⁹ However, the palladium species cannot be re-deposited completely after reaction. One potential strategy to design the stable heterogeneous catalyst for the Heck reaction is to encapsulate the palladium species by using the support as a reservoir to restrict the palladium active species. In this regard, dualporous materials with diverse pore distribution and a certain rigid network structure would be desirable supports, in which the micro pores can form an effective scaffold for the deposition of metal nanoparticles, whereas the rigid structure can protect the collapse of network and restrict the Pd species to prevent their sintering. More interestingly, the Pd NPs encaged in the micro network have an excellent stability compared to the homogeneous and other heterogeneous catalysts.

Previously we have proposed a low-cost strategy to synthesize high surface area microporous knitting aryl network polymers(KAPs) *via* one-step 'knitting' of rigid aromatic compounds blocks with an external crosslinker²⁰. Herein we describe the first preparation of novel dual-porous carbon-supported Pd NP catalysts *via* the carbonization of KAPs-1,3,5-triphenylbenzene (C-(KTB-Pd)), KAPs-benzene (C-(KB-Pd)) and Chloromethyl Polystyrene Resin(C-(CPR-Pd)) (Scheme 1, see Supporting Information(SI) for experiment details). Pd NPs were generated in these three porous materials, by controlled

carbonization in the presence of palladium precursors and their catalytic applications were evaluated for Heck coupling reactions. The palladium NPs size effect and the optimization of the reaction parameters are addressed, aiming at developing C-(KTB-Pd) as a heterogeneous catalyst with high catalytic activity and selectivity for the Heck coupling reaction. Owing to the large surface area, high microporsity and excellent rigid network properties of KTB, it is an excellent supporting material for Pd NPs. Additionally, the control over the size of Pd NPs and their subsequent effect on their catalytic activity, and the recycling potential of the carbonsupported Pd NPs have all been assessed.



Scheme 1. Synthetic route of microporous carbon supported Pd NPs catalysts.

Experimental Section

Materials: Benzene, FeCl₃ (anhydrous), methanol and 1,2dichloroethane (DCE) were obtained from National Medicines Corporation Ltd. of China, all of which were of analytical grade and were used as received. Chloromethyl Polystyrene Resin (CPR, Aladdin, 100-200 mesh), formaldehyde dimethyl acetal (FDA, Alfa Aesar, 98%) and 1,3,5-triphenylbenzene (Alfa Aesar, 98%) were also used as received.

Preparation of catalysts

In the experiments, KTB (KB) powders as the initial precursors were prepared according to our previous report²⁰. The C-(KTB-Pd) catalyst was prepared using an impregnation method. In a typical synthesis, 10 mg PdCl₂ was dissolved in 2 ml acetonitrile at a flask, after the solution changed to bright yellow, 80 mg of KTB was dispersed in it and mixing for 12h, the suspension was centrifugal separation and washed by acetone for three times. The slurry was dried in an oven at 60°C for 6h, than the resulting powder was heated in a tube furnace at 500°C under flowing N₂ for 4 h, the heating rate is 2°C/min and then

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reduction at 400°C under an H₂ atmosphere for 2h. At last the sample was cooled to room temperature at a N₂ atmosphere. The applied calcination temperatures for C-(KTB-Pd) were varied from 500 to 800 °C for 4h, and then reduction at 400°C under an H₂ atmosphere for 2h. The catalysts C-(KB-Pd) and C-(CPR-Pd) were also prepared following the same procedure, the detals was present in supporting information (ESI). Characterization

Transmission electron microscopy (TEM) was carried out using a FEI Tecnai G2 20 electron microscope running at 200 kV. The average Pd NPs size was calculated by counting over 200 particles. The XRD patterns were obtained on a Bruker Advanced D8 diffractometer over a 20 range of 5-90° with Cu Kα radiation. Pd contents were analyzed by atomic absorptionspectrometry (AAS) on a Perkin Elmer AA-300. X-ray photoelectron spectroscopic (XPS) analysis was carried out on a VG Multilab 2000 spectrometer using Al Kα radiation at apower of 300 W. The pass energy was set at 100 eV, and C1s line at 284.6 eV was used as a reference. All the samples were washed with acetone and dried before XPS characterization. The surface area, N₂ adsorption isotherms (77.3K), and pore size distribution of prepared catalysts were measured using Micromeritics ASAP 2020M surface area and porosity analyzer. Before analysis, the samples were degassed at 110 °C for 8 h under vacuum $(10^{-5}$ bar). The products of the coupling reaction were identified by ¹H NMR spectra using a 400 MHz Bruker AV400 instrument in CDCl₃. Chemical shifts are reported in parts per million (ppm) downfield from TMS.

The Heck coupling reaction

All reactants and solvents (Aldrich/Fluka) were used without further purification or drving. Typically, the Heck reaction was carried out as follows: iodobenzene (1mmol), trihydrate potassium phosphate (1.5 mmol), and styrene (1.2 mmol) were dissolved in dimethyl formamide (DMF) (2ml) contained in a round bottom flask (10 ml) equipped with a reflux condenser. The flask containing the reaction mixture was immersed into an oil bath at a temperature of 120 °C under vigorous stirring for a certain period to preheat the reaction mixture, and then catalyst was added into liquid mixture to initiate the reaction. After the reaction end, the mixture was centrifugal filtration to separate the liquid phase. The product was obtained by preparative TLC using a mixed solution of ethyl acetate and petroleum ether (1:10, v/v) as eluting solvent. The products were characterized and confirmed by ¹HNMR.

For the recycling experiments, 20mg C-(KTB-Pd), 1mmol iodobenzene, 1.2 mmol styrene and 1.5 mmol K₃PO₄·3H₂O were added to 2 ml DMF. The reaction was carried out at 120 °C in air for 2 h. Then the mixture was centrifugal filtration to separated. The obtained catalyst was washed by distilled water and acetone at least three times, dried under vacuum and re-used in the next run.

Results and Discussion

Catalysts characterization

DOI: 10.1039/C5DT02133B ARTICLE

Microporous polymers prepared from different monomers have a remarkable difference in their surface area and rigid structure. When 1,3,5-triphenylbenzene was used as a monomer, the rigidity of the obtained network was far stronger than that prepared using benzene as a monomer. As shown in Table 1 (entry 2), the surface area of KB is $1351 \text{ m}^2 \text{g}^{-1}$ but the ratio of micropores is only 19.8 %, KTB has a 62 % micropore but its surface area is 1059 m²g⁻¹. The CPR has almost no micropores and its surface area is 24m²g⁻¹. The presence of the micropores is very useful to contain and immobilize smaller Pd NPs. The Pd NPs are confined in the Table 1. The catalysts properties and activity comparison of three catalysts

| Entry | Sample | S _{BET} ^a m ² /g | MP ^b % | Pd wt% | average diameter ^c nm | Yield % |
|-------|------------|--|----------------------|-----------|--|------------|
| 1 | КТВ | 1059 | 62.0 | - | - | - |
| 2 | КВ | 1351 | 19.8 | - | - | - |
| 3 | CPR | 24 | 7.9 | - | - | - |
| 4 | C-(KTB-Pd) | 924 | 58.3 | 1.1 | 4 | 96 |
| 5 | C-(KB-Pd) | 775 | 21.4 | 0.98 | 7 | 92 |
| 6 | C-(CPR-Pd) | 439 | 31.9 | 0.81 | 16 | 62 |
| | | | | | | |

^aSurface area calculated from N₂ adsorption isotherms at 77.3K using BET equation. ^bMicroporous proportion calculated from Pore volume and Micropore volume. ^caverage diameter was counted over 200 particles in different areas of the sample ^dIsolated yield. Reaction conditons: were counted. iodobenzene, styrene, K₃PO₄·3H₂O, 10 mg catalysts, DMF 2ml, T=120°C and reaction time 2 hours.

micropores cavities and cannot diffuse out due to their size limitation to cross the micropores. But MOPs with meso-/macro structure are less appropriate candidates to act as hosts because the Pd NPs can freely move through the channels and eventually can interact with other Pd NPs to grow further or migrate out of the porous supports.

After carbonization at a certain temperature (500°C), the surface area of three catalysts changed to 775 and 924 m^2g^{-1} respectively (Table 1, entry 4-5). The degree of the decreased surface area obviously complies with the rigid network and microporous structure of these materials. So the Pd NPs also couldn't grow larger even during carbonization due to their confinement in the micropores of these materials carbonization. However, the surface area of C-(CPR-Pd) has increased to 439 m²g⁻¹, we considered the Chloromethyl Published on 19 June 2015. Downloaded by University of Queensland on 23/06/2015 17:11:27

Polystyrene Resin (CPR) is rich in macroporous, when carbonization at high temperature, the collapse and decomposing of part structure result in abundant micro/ meso pore greatly increase the surface area.²¹

TEM images show a uniform size distribution of Pd NPs with near spherical morphology encaged in the novel micro carbon materials (Figure 1), with an average diameter of 4, 7, 16 nm for C-(KTB-Pd), C-(KB-Pd), C-(CPR-Pd), respectively. It was also observed that C-(KB-Pd) contains uniform and smaller Pd NPs than those generated in C-(CPR-Pd) (Figure 1 e, f). Moreover, the average size of palladium particles can be tuned in the range of 4-6 nm (Figure1 d) on C-(KTB-Pd). The results agree with the greater microporosity of C-(KTB-Pd), and the protection of microsporous and rigid network. These properties prevent the collapse of catalyst and keep the Pd NPs apart with a better dispersion and smaller size. The results demonstrate that the pore structure has a strong influence on the growth of Pd NPs during carbonization, the smaller, narrower pore distribution and strong rigid network leads to the generation of smaller Pd NPs.



Figure 1. TEM images and the particle size distribution of Pd nanoparticles supported on three microporous carbon. a) C-(KTB-Pd). b) C-(KB-Pd). c) C-(CPR-Pd)

The influence of temperature on the Pd NPs size is shown in Figure S1 (ESI). The picture a clearly shows the encapsulation of Pd NPs by porous carbon, and b, c, d show the different Pd NPs size of the sample C-(KTB-Pd) at different carbonization temperature. During the use of NPs embedded inside porous materials as heterogeneous catalysts, one of the key points to be addressed is their stability. Compared to MOFs, MOPs have a better thermal stability. When the calcination temperature is increased from 500 to 800 °C, the average diameter of Pd NPs is increased from 4 to about 50 nm, and the surface area is reduced to $713m^2g^{-1}$ (Table 2. Entry

The porous properties of three catalysts were analysed by N₂ sorption analysis. As shown in Figure 2(a), the adsorption isotherms of all three catalysts indicate a steep N₂ gas uptake at low relative pressure (P/P₀< 0.001), thus indicating an extensive micropore structure. The flat course in the intermediated section is a typical type I feature according to the IUPAC classification. At higher relative pressures, however, the isotherms for the three catalysts differed quite markedly. The N₂ isotherm for C-(KTB-Pd) is very similar to our previously reported catalyst²⁰ and can be classified as Type I. The isotherm of C-(CPR-Pd) exhibits more Type II character and displays pronounced pore filling at high relative pressures, which is in consistent with the presence of larger pores that allow unrestricted multilayer adsorption.²³ The isotherm for C-(TB-Pd) can also be classified as Type II but with evidence of Some Type IV character, only a small degree of hysteresis was

Table 2. The catalytic activity comparison of different carbonization temperature

| Entry | Temperature | S_{BET}^{a} | Average particles(nm) | | Yield |
|-------|-------------|---------------|-----------------------|------------------|------------------|
| | °C | m²/g | HRTEM ^b | XRD ^c | (%) ^d |
| 1 | 500 | 924 | 4.0 | 7.6 | 96 |
| 2 | 600 | 810 | 10.3 | 16.2 | 90 |
| 3 | 700 | 722 | 17.6 | 25.4 | 60 |
| 4 | 800 | 713 | 48.7 | 45.6 | 17 |
| | | | | | |

^aSurface area calculated from N₂ adsorption isotherms at 77.3 K using BET equation. ^b Over 200 particles in different areas of the sample were counted. ^cCalaulated from the Scherrer Formula. ^dIsolated yield. Reaction conditons: iodobenzene, styrene, K_3PO_4 ·3H₂O, 10 mg catalyst, DMF, T=120 °C and t = 2h.



Figure 2. (a) Nitrogen adsorption isotherm and desorption isotherm at 77.3 K. (b) pore size distribution of three catalysts.

observed upon desorption, indicating the presence of mesopores and macropores. From the pore size distribution data (Figure 2(b)), we conclude that the microporosity and rigid structures are in favor of the formation of small Pd NPs. The catalyst C-(KB-Pd) and C-(CPR-Pd) has some micropores,

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but compared to the mesopores and macropores, it is very a small proportion. The average pore size of C-(KTB-Pd), C-(KB-Pd), C-(CPR-Pd) are 2.6, 4.9 and 4.5 nm respectivily, calculated from $4VA^{-1}$ and the pore size distribution of catalysts were calculated using DFT methods.

The high angle XRD patterns of the Pd NPs supported on microporous carbon with different carbonization temperature are shown in Figure 3. The typical diffraction pattern of palladium *fcc* crystalline structure is clearly observed. The diffraction peaks become sharper and more intense with the increased temperature, suggesting an increased crystalline domain size, which is in consistent with the TEM results (Table 2). The increasing crystalline domain size is due to the enhanced aggregation of palladium clusters or particles at a higher temperature (800 °C) during carbonization process.



Figure 3. High angle XRD patterns of the Palladium support microporous carbon C-(KTB-Pd) at different carbonization temperature. a) 500°C, b) 600 °C, c) 700 °C, d) 800 °C.

In order to get an insight into oxidation state of palladium in C-(KTB-Pd), X-ray photoelectron spectroscopy (XPS) experiments were performed (Figure S2 ESI). The result displays the binding energy of Pd 3d for C-(KTB-Pd). It exhibits two observable peaks centred at 335.75 and 341.05 eV, which are assigned to Pd $3d_{5/2}$ and Pd $3d_{3/2}$, respectively. This result implies zero oxidation state of Pd.

Based on the above results, we successfully tuned the size of Pd NPs in the range of 4-20 nm on porous carbon supports. Moreover, the average size of palladium particles can be controlled at 4 nm by controlling the porous structure and calcination temperature.

Catalytic activity of catalyst C-(CKB-Pd)

The Heck reaction has been proved to be structure sensitive when catalysed by metal nanoparticles based catalysts. The trend is attributed to the fact that smaller Pd NPs possess a higher catalytic efficiency. In the present study, the size of C-(KTB-Pd) supported Pd NPs is varied by applying different carbonization temperature and controlling the pore diameter distribution of the support. The results are shown in Table 1 and Table 2 indicating that smaller Pd NPs are more active to get the desired products in Heck coupling reactions. The product yield increases with a decrease in the size of the Pd NPs. The highest yield was obtained with Pd NPs with an average diameter of 4-6 nm, while the lowest yield was obtained with palladium particles of about 50 nm diameters (Table 2, entry 4).

Table 3 The effect of solvents and base^a

| Entry | Solvent | Base | т (°С) | Yield (%) ^b |
|-----------------|------------------|--------------------------------------|--------|------------------------|
| 1 | DMF | K ₃ PO₄·3H ₂ O | 120 | 96 |
| 2 | DMF | K ₃ PO₄·3H ₂ O | 100 | 74 |
| 3 | DMF | K ₃ PO₄·3H ₂ O | 80 | 55 |
| 4 | DMF | Na ₂ CO ₃ | 120 | 37 |
| 5 | DMF | EtONa | 120 | 95 |
| 6 | DMF | Cs ₂ CO ₃ | 120 | 12 |
| 7 | DMF | KOt-Bu | 120 | 94 |
| 8 | DMF | КОАс | 120 | 62 |
| 9 | DMF | NaHCO ₃ | 120 | 93 |
| 10 | DMF | NaOAc·3H ₂ O | 120 | 94 |
| 11 | DMF | K ₂ HPO ₄ | 120 | 32 |
| 12 | DMF | K ₂ CO ₃ | 120 | 88 |
| 13 | DMAc | K ₃ PO₄·3H ₂ O | 120 | 85 |
| 14 | H ₂ O | K ₃ PO₄·3H ₂ O | 120 | 12 |
| 15 | EtOH | K ₃ PO₄·3H ₂ O | 120 | 74 |
| 16 | Toluene | K ₃ PO₄·3H ₂ O | 120 | 89 |
| 17 | cyclothexane | K ₃ PO₄·3H ₂ O | 120 | 73 |
| 18 | DMSO | K ₃ PO₄·3H ₂ O | 120 | 92 |
| 19 | NEt ₃ | K ₃ PO₄·3H ₂ O | 120 | 78 |
| 20 ^c | DMF | K₃PO₄·3H₂O | 120 | 95 |
| 21 ^d | DMF | K ₃ PO₄·3H ₂ O | 120 | 95(76) |

^aReaction conditons: 10 mg of C-(KTB-Pd), 1 mmol of iodobenzene, 1.2 mmol of styrene, 1.5 mmol of base, 2 ml of solvent, 120 °C, 2h in air. ^bIsolated yield. ^CN₂ atmosphere. ^dCommercial 5% Pd/C as catalyst, and the yield in parentheses is the second runs.

In order to evaluate the catalytic performance of C-(KTB-Pd), the Heck reaction of aryl halides and olefins were studied. First, we examined the activity of C-(KTB-Pd), C-(KB-Pd), C-(CPR-Pd). As shown in Table 1, using 0.1mol % Pd with respect to iodobenzene, C-(KTB-Pd) gave a 96% yield within 2h at 120 °C (Table 1, entry 4), showing obvious advantage over C-(KB-Pd) and C-(CPR-Pd) in the controlled experiments (Table 1, entry 5, yield 92% and enrty 6, yield 62%). Table 2 (entry 1-4) illustrates that the higher carbonization temperature results in the production of larger Pd NPs. The smallest Pd NPs gave the highest yield (Table 1, entry 1). So we selected the C-(KTB-Pd) carbonization at 500°C as the catalyst for the reactions reported in this article. The influence of temperature, base, and solvent on catalytic property of C-(KTB-Pd) was systematically investigated by using the coupling of

DOI: 10.1039/C5DT02133B Journal Name

iodobenzene and styrene as a model reaction. The results are summarized in Table 3.

Table 4. The Heck coupling reaction of different aryl halides with different alkenes over C-(KTB-Pd)^a

$$R - F_{I} + F_{I} - R_{I} - \frac{C - (KTB-Pd base)}{DMF 120 \circ C} R - F_{I}$$

 $R_1 = H, CH_3, n-Bu, Cl$

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^aReaction conditions: 10 mg of C-(KTB-Pd), 1 mmol of iodobenzene, 1.2 mmol of styrene, 1.5 mmol of base, 2 ml of solvent, 120 °C in air. ^bIsolated yield in parentheses. ^c 140 °C.

The reaction temperature has a significant effect on the C-(KTB-Pd) activity. With increasing reaction temperature, yield increased from 55% to 96% (Table 3, entries 1-3) and the highest catalytic activity was achieved at 120 C (Table 3, entry 1). The effect of base is shown in Table 3 (Entries 4-12) and the result shows the stronger base gave the higher yield, Table 3 (Entries 5, 7, 10), and $K_3PO_4 \cdot 3H_2O$ is found to be the best base for this purpose. The solvent used in the Heck reaction also has a great influence on theC-(KTB-Pd) activity, as shown in Table 3 (Entry 13-19). It is observed that the suitable solvent is N, N-Dimethyl formamide (DMF) and Dimethyl sulfoxide (DMSO) resulting in a 96% and 92% yield, respectively (Table 3, entries1 and 18). In water, ethanol and cyclohexane (Table 3, entry14-15, 17), the catalytic activity is low. More interestingly, the change in the reaction environment from inert to ambient had no negative effect on activity of C-(KTB-Pd) activity (Table 3, entry20). Generally, homogeneous catalysts (usually with P and N ligands) used in the Heck reactions are very sensitive to the presence of air during the reaction,²² C-(KTB-Pd) catalyst would be more suitable for practical applications of such catalysts. We also compared the catalytic efficiency with commercial Pd/C (5% wt) catalyst. Thought it give high yield in first run (table 3, entry 21), the yield decrease to 76% in second runs.

Reactivity for various substrates of catalyst C-(KTB-Pd)

To examine the scope for utilization of C-(KTB-Pd) in the Heck reaction, a variety of aryl halides were coupled with different olefins in DMF in the presence of 10 mg C-(KTB-Pd) using K_3PO_4 · $3H_2O$ as a base. The results are summarized in Table 4. For iodobenzene and other aryl iodides with substituents such as $-CH_3$ and $-OCH_3$, good yields (80-90%) of the products were observed within 2-4 h (Table 4, entries 1–11). Further study indicated that aryl iodides with larger steric bulk also shows a high activity with aryl styrene (Table 4, entrys12-17). Aryl bromides are difficult to be activated compared to aryl iodide, probably because of stronger C-Br bond. As a result, the coupling reactions of aryl bromides with different olefins required higher temperature and extended reaction times even in the presence carbon supported Pd NPs (Table 4, entry 17-18).

We also adopted a hot filtration experiment to determine if the heterogeneous or the dissolved homogeneous Pd species were the real catalysts responsible for the reaction between iodobenzene and styrene. After 30 minutes, we stopped the reaction immediately and remove the solid catalyst from the reaction mixture. The yield obtained was 38%. The mother liquor was allowed to react for another 90 minutes under the same conditions but the final yield was 38.6%, no obvious increase in yield was observed, and the Pd content of the mother liquor was 2.2 ppm according to AAS. The results indicate that there only little Palladium species leached and the active phase was not the dissolved palladium species leached from the supports.

Recycle performance comparison of three catalysts.

Another important issue concerning the use of a solid catalyst is its reusability and stability under reaction conditions. To gain insight into this issue, the recycling studies were performed for the Heck coupling reaction, by regenerating and then reusing the catalyst under the same conditions (Figure 4).

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Before reuse, the solid was separated by filtration and washed with water and acetone several times. Almost similar products yield (95%) was achieved after 10 recycling experiments of catalyst C-(CTB-Pd), and the TEM images (Figure S3 ESI) of the reused catalyst clearly show no significant change in the size of Pd NPs on porous carbon supports after the reaction. These results thus illustrate the high stability and excellent reusability of the catalyst. We also take kinetic study to research the recycle performance of catalyst C-(KTB-Pd), (Fig S4 ESI) the result review the catalyst run 5 also give a good yield in 2 hours, probably we not rely on expend reaction time to improve the yield.



Figure 4. Recycling test of three catalysts, Reaction conditions: 20 mg of C-(KTB-Pd), 1 mmol of iodobenzene, 1.2 mmol of styrene, 1.5 mmol of K_3PO_4 · $3H_2O$, 2 ml DMF, 120 °C, 2h in air.

Conclusions

The study encompasses the first description and simple preparation of C-(KTB-Pd) catalysts through the method of direct carbonization and reduction. The prepared palladium nanoparticles were in the form of near spherical particles of <6nm diameter, the size being adjustable by changing the carbonization temperature and different porous materials. High dispersed C-(KTB-Pd) catalyst not only has high activity for Heck coupling reactions, but also offers many promising advantages such as stability at relative high temperatures, insensitivity to oxygen, total separation from the reaction products and reusability. C-(KTB-Pd) would be suitable catalysts for Heck coupling reactions, given the current interest in novel porous carbon and the scarcity of reusable solid catalysts.

Acknowledgements

We acknowledge the Opening Foundation of Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, South-Central University for Nationalities and the spectroscopic analysis conducted at the Analytical and Testing Centre, Huazhong University of Science and Technology, Wuhan, China. This work was financially supported by National Natural Science Foundation of China (No. 21473064/ 21474033/ 51273074)

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