



A titania-supported highly dispersed palladium nano-catalyst generated via in situ reduction for efficient Heck coupling reaction

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ABSTRACT

Supported metal catalysts have been applied in many current industrial processes. The dispersion of metal particles on solid supports has been proven to affect the performance of catalysts greatly. In this study, a titania-supported palladium catalyst prepared by a simple pH-controlled adsorption method is efficient and recyclable for the Heck coupling reaction of aryl halides and alkenes. The pH-controlled adsorption method results in high dispersion of palladium species on titania surface. During the reaction, palladium nanoparticles are in situ generated via reduction on the surface of titania. TEM images indicate that the nanoparticles are nearly monodisperse in size. Recycling studies have shown that the catalyst can be readily recovered and reused several times without significant loss of catalytic activity.

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1. Introduction

The cross-coupling reaction of aryl or vinyl halides with alkenes, that is, Heck reaction, is among the most commonly used methods for C–C bond formation and widely applied to organic and fine-chemical synthesis [1–4]. In the past few years, the development of ligands has provided highly active homogeneous palladium catalysts for Heck reactions under mild conditions and enabled using a wide range of aryl halides [1,4]. However, homogeneous processes suffer from the problems concerning separation from reaction mixture, reuse of expensive palladium catalysts. In addition, most of ligands for Heck reactions are undesirable in the industrial chemistry because of their toxicity, high price and air-sensitivity.

In principle, the use of supported palladium catalysts could address some of these problems mentioned above. Thus, the practical applications of Heck reactions have greatly driven the need for the development of recyclable and efficient heterogeneous palladium catalysts [5–10]. In this regard, supported palladium catalysts exhibit particularly promising performances for the Heck reaction. A variety of solid materials as supports have been investigated, for example, active carbon [11], mesoporous silica [12], metal oxides [13–16], zeolites [17,18], magnetic materials [19], hydrotalcites [20], hydroxyapatite [21], and organic–inorganic hybrid materi-

als [22]. Traditionally, supported palladium catalysts are typically prepared by impregnation these solid supports with a palladium salt aqueous solution, followed by drying or calcination in air and reduction. The resultant palladium particles are usually randomly dispersed on the surface of support with broad size distribution, which may cause a decrease in catalytic performance. Therefore, preparation of supported palladium catalysts with high dispersion and narrow size distribution of palladium particles becomes particularly desirable for the improvement in catalytic performance.

Very recently, a highly dispersed palladium catalyst supported on ordered mesoporous silica–carbon composites was reported to be highly active and reusable in the Heck reaction [10] probably because the high dispersion of palladium species on the surface of support could prevent formation of catalytically deactivated palladium black and keep all active palladium species available for the reaction [9]. The increase in catalytic activity and reusability for highly dispersed catalyst would allow use of low palladium loading for achieving efficient turnover and thereby reduce the cost of products in large-scale processes. In addition, a simple and efficient adsorption method has appeared as an attractive approach to highly dispersed palladium on γ -Al₂O₃ [23], in which palladium content can be tuned by varying pH value of aqueous solution and palladium(II) concentrations in the adsorption stage.

As a typical metal oxide, TiO₂ usually shows pH-dependent surface charges when it is immersed in aqueous solution because of the existence of Ti–OH on the surface. The adsorption property of TiO₂ greatly changes with environment of different pH value. In

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this paper, we report the high catalytic performance of the highly dispersed Pd on TiO₂ catalyst prepared by the adsorption method for the Heck cross-coupling reaction of aryl halides and alkenes. The method represents a simple and efficient approach to highly dispersed catalysts. Moreover, we demonstrate that this heterogeneous catalyst can be readily recovered and reused several times without significant loss of activity.

2. Experimental

2.1. General

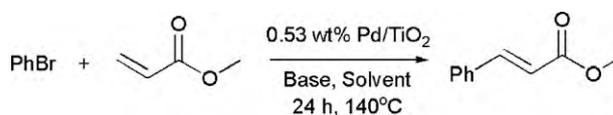
Commercially Titania P-25 (TiO₂, 80% anatase 20% rutile, BET surface area: 53 m² g⁻¹) was provided by Degussa. PdCl₂ (AR) was obtained from Shanghai July Chemical Co. Ltd. and used as received. Solvents were obtained from Sinopharm Chemical Reagent Co. Ltd and purified prior to use. Other chemicals were purchased from Sigma–Aldrich or Alfa Aesar and used without further purification or drying. Water used in the experiments was deionized (DI) and doubly distilled prior to use. Unless otherwise stated, all experiments were performed in nitrogen atmosphere.

2.2. Catalyst preparation

Pd/TiO₂ catalysts prepared by an adsorption method (Pd/TiO₂-ads) were prepared by the following procedures: 2.0 g of TiO₂ was added to 60 mL aqueous solution of PdCl₂ (0.03 mol/L), of which different pH was adjusted by 2 M HCl aqueous solution. The suspension was then vigorously stirred for 2 h at room temperature. After the adsorption, the powdery solid was separated by filtration and washed for several times with a large amount of water until no Cl⁻ could be detected in the filtrate by AgNO₃ aqueous solution, followed by drying at 120 °C overnight and calcination in air at 500 °C for 3 h. The resulting light yellow solid powder was cooled to room temperature and stored in a vacuum desiccator. For comparison, the 0.26 wt% Pd/TiO₂ catalyst was prepared by a conventional wet impregnation method (Pd/TiO₂-imp). TiO₂ was added into a PdCl₂ aqueous solution without pH adjustment and the mixture was evaporated to dryness at 60 °C. The resultant powdery solid was further dried at 120 °C and finally calcined in air at 500 °C for 3 h. The resulting solid powder was cooled to room temperature and stored in a vacuum desiccator.

2.3. Characterization

Inductively coupled plasma (ICP) analyses of the content of Pd in each solid catalyst sample and the filtrate after the reaction were performed on an Ultima 2 analyzer (Jobin Yvon). Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max RA diffractometer with Cu K α radiation at 40 kV and 40 mA with a scan speed of 2° min⁻¹ and a range of 2 θ from 10° to 80°. The morphology, structure and EDX spectra of catalyst were analyzed on a JEOL 2010 transmission electron microscope (TEM) with energy dispersive X-ray (EDX) spectrometer. The sample for TEM analysis was prepared by placing a drop of the suspension in ethanol onto a continuous carbon-coated copper TEM grid and dried at room temperature under atmospheric pressure. For the sample, more than 100 particles from different parts of the grid were used to determine the particle size distribution. X-ray photoelectron spectroscopy (XPS) measurements were analyzed on coated alumina with a physical Electronics PHI-Quantum 2000 Scanning ESCA Microprobe using Al K α radiation (1846.6 eV) as X-ray source to investigate the oxidation state of Pd before and after reaction. Diffuse reflectance UV–Vis reflectance spectra of the samples in the



Scheme 1. Heck reaction between bromobenzene and methyl acrylate.

wavelength range of 300–800 nm were measured by a Lambda-900 spectrophotometer with an integrating sphere, and BaSO₄ was used as a reference sample.

Unless otherwise stated, product yields from the Heck reaction were determined by column chromatography. GC analysis was measured by a Varian 430 Gas Chromatograph using a 3-m length column packed with DC-200 stationary phase. ¹H and ¹³C NMR spectra were recorded using a Burkert Avance 400 spectrometer using CDCl₃ as solvent.

2.4. Catalytic reactions

In a typical reaction, 0.26 wt% Pd/TiO₂-ads catalyst (0.10 g, 0.5 mol% Pd relative to bromobenzene), bromobenzene (0.5 mmol), methyl acrylate (0.6 mmol), and KOAc (0.6 mmol) were added to a pressure tube, followed by addition of DMA 2 mL under nitrogen atmosphere. The tube was sealed and the mixture was allowed to stir in a preheated oil bath at 140 °C for 24 h. After the reaction was completed, the solid catalyst was separated by centrifuge, washed with water to remove base and salt and finally with acetone to remove adsorbed organic substrate, followed by drying at 120 °C and activated at 250 °C under vacuum (2 Torr) for 2 h prior to being reused. The filtrate was diluted by water followed by extraction with ethyl acetate (3 × 10 mL). The combined organic phase was washed with water (2 × 10 mL) and brine (10 mL), and dried over anhydrous Na₂SO₄. The solvent was removed and the resultant residue was purified by column chromatography (SiO₂, ethyl acetate/hexane gradient). The product was dried under vacuum, weighed and characterized by ¹H and ¹³C NMR spectroscopy. To study heterogeneity of the Heck reaction, a hot filtration test was also adopted. After 5 h of reaction time the 0.26 wt% Pd/TiO₂-ads solid catalyst was filtered by hot filtration under nitrogen atmosphere and the hot filtrate was further reacted with fresh KOAc (0.6 mmol) at 140 °C for additional 10 h. After the reaction, the samples of the reaction mixture were analyzed by GC and ICP.

3. Results and discussion

3.1. Heck reaction catalyzed by catalysts with different palladium content

Initially, Heck reaction of bromobenzene and methyl acrylate was chosen as a model reaction (Scheme 1) with 0.53 wt% Pd/TiO₂-ads catalyst that was prepared when the pH value of aqueous solution of PdCl₂ was 2. Bases, solvents, and loadings of the catalyst were screened to optimize reaction conditions (Table 1). The effect of bases in the reaction was observed. Alkali carbonates gave low or moderate yields (entries 1–3) and K₃PO₄ gave a lower yield (entry 4). When organic base Et₃N was used, the moderate product yield (39%) was obtained (entry 7). Gratifyingly, the use of KOAc dramatically improved the yield (79%) (entry 6). DMA was found to be more effective than other solvents such as DMF, DMSO and NMP (entry 6 and entries 11–13). Reducing the amount of the catalyst loading from 0.5 mol% to 0.25 mol% or 0.1 mol% led to decrease in yields (entries 8 and 9). The oxidative conditions seriously inhibited the desired reaction, as indicated by the reaction performed under air or oxygen atmosphere (entries 14 and 15). In addition, the time dependence of the yield under the optimized condition is shown in Fig. 1. It is clear that the reaction of bromobenzene

Table 1
Optimization of the Heck reaction of bromobenzene and methyl acrylate using 0.53 wt% Pd/TiO₂-ads catalyst.^a

Entry	Pd (mol%) ^b	Base	Solvent	Yield (%) ^c
1	0.5	Na ₂ CO ₃	DMA	40
2	0.5	K ₂ CO ₃	DMA	45
3	0.5	CS ₂ CO ₃	DMA	10
4	0.5	K ₃ PO ₄	DMA	23
5	0.5	NaOAc	DMA	70
6	0.5	KOAc	DMA	79
7	0.5	Et ₃ N	DMA	39
8	0.25	KOAc	DMA	69
9	0.1	KOAc	DMA	50
10	0	KOAc	DMA	0
11	0.5	KOAc	DMF	54
12	0.5	KOAc	DMSO	42
13	0.5	KOAc	NMP	70
14 ^d	0.5	KOAc	DMA	35
15 ^e	0.5	KOAc	DMA	5

^a Reaction conditions: bromobenzene (0.5 mmol), methyl acrylate (0.6 mmol), base (0.6 mmol), solvent (2 mL), 24 h, 140 °C, under N₂.

^b The ratio of absolute amount of Pd loading to bromobenzene.

^c Isolated yields.

^d Under air.

^e Under O₂, GC yield.

with methyl acrylate took about 24 h for completion. There was an induction period of about 3 h, after which the reaction proceeded rapidly during the following period.

Considering that the catalytic properties of supported catalysts depend on their preparation conditions, we further evaluated the catalytic performance of Pd/TiO₂ catalysts obtained at different pH values in a fixed 0.03 mol/L PdCl₂ aqueous solution. Palladium content in the Pd/TiO₂ can be regulated by varying pH value of PdCl₂ aqueous solution. When the pH value was lower than the identical electric point (IEP = 6.25) of TiO₂ [24], the surface would be transferred to = Ti-OH₂⁺ and the absorption of Pd could easily occur on the surfaces via coulombic interactions. As shown in Fig. 2, Pd content on TiO₂ increased when the pH value was increased. Interestingly, the catalyst containing 0.26 wt% palladium, which was prepared when the pH value was 1.5, exhibited the best activity for the Heck reaction of bromobenzene with methyl acrylate under a fixed ratio of Pd/bromobenzene using optimized conditions while catalysts containing higher Pd content were less active. It is reasonable to speculate that a higher Pd content may lead to the agglomeration of Pd species after the calcination or during the reaction. Thus, highly dispersed Pd species on the surface of TiO₂

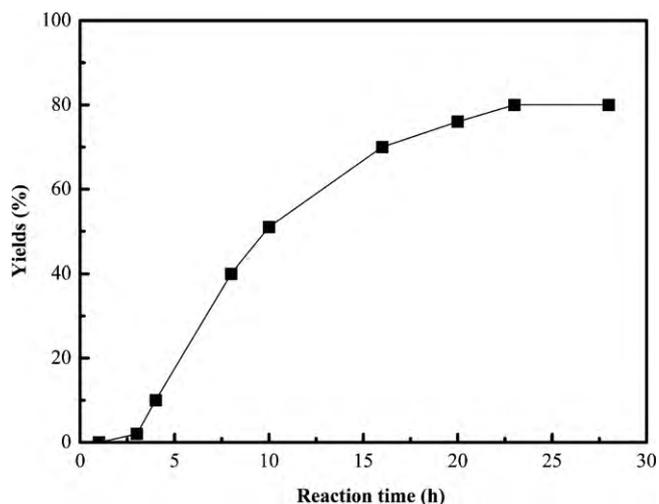


Fig. 1. Time of yield plot for the Heck reaction in the presence of 0.53 wt% Pd/TiO₂-ads as catalyst.

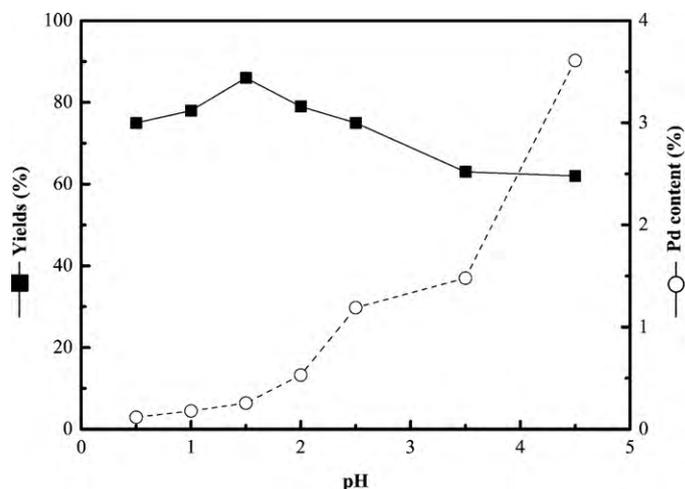
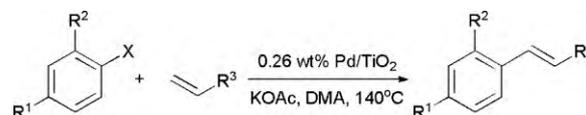


Fig. 2. Effect of pH value and Pd content on catalytic properties of the Pd/TiO₂ catalyst for Heck reaction (optimized conditions).



Scheme 2. Heck reaction between aryl halides and alkenes.

may account for the high catalytic performances of the sample with an appropriate Pd content. The relatively lower yield at a much lower Pd content (<0.26 wt%) probably suggests that the interaction existing between Pd species and TiO₂ might cause the decrease in catalytic performance. The use of the 0.26 wt% Pd/TiO₂-ads catalyst led to exclusive formation of *trans*-methyl cinnamate in 86% isolated yield.

3.2. Heck reaction of aryl halides with alkenes catalyzed by 0.26 wt% Pd/TiO₂

The scope of the reaction (Scheme 2) was explored under the optimized reaction conditions with 0.26 wt% Pd/TiO₂-ads catalyst. As shown in Table 2, a range of aryl iodides, aryl bromides and even activated aryl chlorides could undergo Heck reaction to produce exclusively *trans* products in moderate to excellent yields. Aryl halides with electron-withdrawing substituents in the *para* positions reacted smoothly (entries 1, 7, 9, 11, and 12), while

Table 2
Heck reaction of aryl halides with alkenes catalyzed by 0.26 wt% Pd/TiO₂-ads catalyst.^a

Entry	X	R ¹	R ²	R ³	Time (h)	Yield (%) ^b
1	I	CH ₃ CO	H	Benzene	10	96
2	I	OCH ₃	H	COOMe	10	93
3	Br	H	H	COOMe	24	86
4	Br	CH ₃	H	COOMe	24	65
5	Br	H	CH ₃	COOMe	24	56
6	Br	OCH ₃	H	COOMe	24	50
7	Br	COOEt	H	COOMe	24	94
8	Br	H	H	Phenyl	24	92
9	Br	CH ₃ CO	H	Phenyl	24	95
10	Br	H	H	CO ₂ i-Bu	24	83
11 ^c	Cl	COOEt	H	COOMe	36	64
12 ^c	Cl	CH ₃ CO	H	Phenyl	36	60
13 ^c	Cl	H	H	COOMe	36	27

^a Reaction conditions: aryl halide (0.5 mmol), alkene (0.6 mmol), base (0.6 mmol), Pd/TiO₂ (0.5 mol%), DMA (2 mL), 140 °C, under N₂.

^b Isolated yields.

^c 150 °C, Addition TBAB (0.3 mmol).

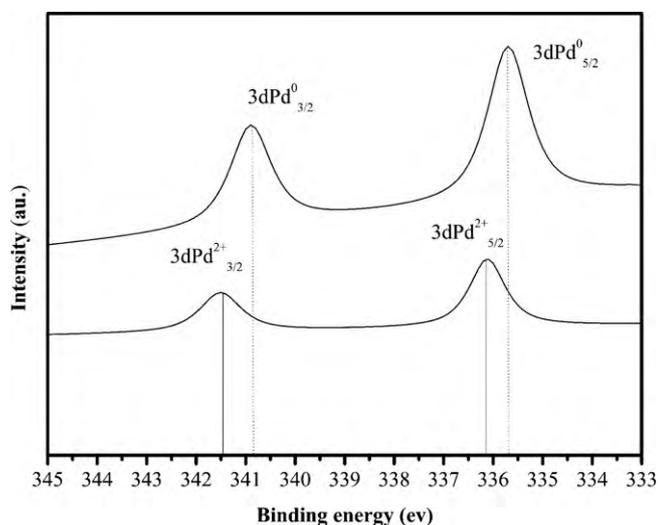


Fig. 3. XPS spectra of 0.26 wt% Pd/TiO₂-ads catalyst (A) before the reaction and (B) after the induction period.

aryl halides with electron-donating substituents were less reactive (entries 4–6). In addition, *ortho*-substituted aryl bromides also provided the desired product (entry 5). We were pleased to find that this catalyst system can couple activated aryl chlorides in the presence of 0.3 mol tetrabutylammonium bromide (TBAB), finishing a synthetically useful yield (entries 11 and 12). Deactivated chlorobenzene also participated in this reaction, albeit in a substantially comparable yield (entry 13). With respect to alkenes, styrene and *i*-butyl acrylate served as suitable coupling partners (entries 1, 8–10, and 12). It should be noted that, the reaction could be scaled up, as exemplified by the coupling reaction of bromobenzene with methyl acrylate 5.0 mmol scale that gave a yield comparable to that on 0.5 mmol scale.

3.3. Characterization of the catalysts

Powder X-ray diffraction (XRD) analysis indicated that the 0.26 wt% Pd/TiO₂-ads solid sample mainly comprised anatase with minor rutile (S1), in agreement with its UV–Vis diffuse reflectance spectrum (S2) in which the intense absorption band centered at 380 nm could be assigned to the intrinsic band gap absorption of anatase [25]. Although no Pd species could be detected by XRD and UV–Vis diffuse reflectance due to low amount of Pd content or its high dispersion, the presence of Pd species in this solid sample was clearly evidenced by X-ray photoelectron spectroscopy (XPS). Fig. 3 shows the XPS spectra of the region corresponding to the binding energy range of 333–345 eV, which included Pd 3d_{5/2} and Pd 3d_{3/2} peaks. Two peaks located around 336.1 eV and 341.4 eV, a characteristic of the electron binding energy of Pd(II) in the 3d_{5/2} and 3d_{3/2} level [26–27]. When Pd content on the surface of TiO₂ was increased, a broad band between 450 nm and 550 nm owing to a d–d transition of Pd(II) species could be obviously observed through UV–Vis diffuse reflectance spectrum [28].

Before reaction, for the 0.26 wt% Pd/TiO₂-ads solid sample, no PdO or Pd particles could be discerned in the TEM images, suggesting that Pd species was likely highly dispersed on the surface of TiO₂. However, inspection of the TEM images of isolated 0.26 wt% Pd/TiO₂-ads catalyst samples after the induction period (3 h) in the reaction of bromobenzene and methyl acrylate indicated the involvement of Pd nanoparticles. Fig. 4 displays the TEM image, corresponding size distribution and EDS spectra of the isolated catalyst. Evidently, highly dispersed spherical metallic Pd nanoparticles with the size of 5–6 nm on the TiO₂ surface were observed.

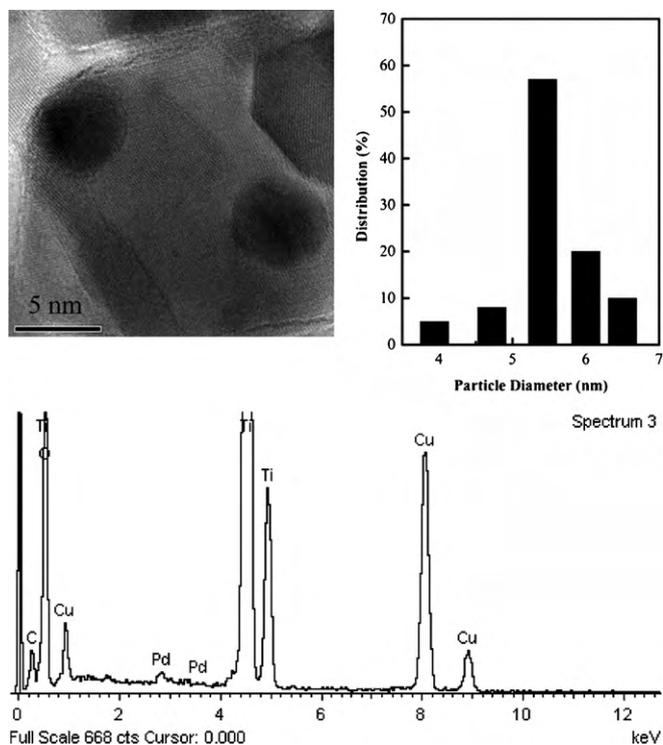


Fig. 4. TEM image, size distribution and EDS spectra of 0.26 wt% Pd/TiO₂-ads catalyst after the induction period.

To gain more information about the nature of the isolated catalyst, a thin film of the same isolated catalyst was prepared and studied using XPS. As shown in Fig. 3, the peaks located around 335.7 eV and 340.9 eV were assigned to the Pd 3d_{5/2} and Pd 3d_{3/2} level in the Pd(0) metallic form in agreement with literature report [29]. The binding energy clearly showed the fact that the Pd nanoparticles in our isolated catalyst contained only Pd(0) species. The above phenomena support that the Heck reaction proceeds via the traditional Pd⁰/Pd²⁺ cycle but not via the Pd²⁺/Pd⁴⁺ mechanism.

It is essential to verify that the catalytic activity is caused by solid Pd/TiO₂ rather than the leached palladium species. In the Heck reaction of bromobenzene and methyl acrylate, the 0.26 wt% Pd/TiO₂-ads solid catalyst was removed by hot filtration at 19% GC yield under nitrogen atmosphere, and the filtrate was further reacted with fresh KOAc at 140 °C for 10 h. The above treatment of the filtrate gave no coupling product. Pd leaching was negligible and the concentration of Pd in the filtrate was less than 0.2 ppm, as found by ICP analysis. This observation, in connection with the fact that the Pd nanoparticles initially generated by in situ reduction did not change during the reaction, suggested that catalytic process might occur on the surface of Pd nanoparticles, although we cannot rule out the homogeneous process [30].

3.4. Reusability of the catalyst

For practical application in the Heck reaction, the lifetime of the heterogeneous catalysts and their reusability are very important factors.

We have carried out recycling uses of the 0.26 wt% Pd/TiO₂-ads catalyst for the Heck reaction between 4-iodoanisole and methyl acrylate, the coupling product was obtained with a yield of 92% in the first cycle. The solid catalyst can be separated readily from the reaction mixture by centrifuge, washed and dried at 250 °C under vacuum for 2 h. The recycled catalyst was then used in the model reaction under the same reaction conditions giving 90%, 94%, 91%, and 89% isolated yield for the first, second, third and fourth

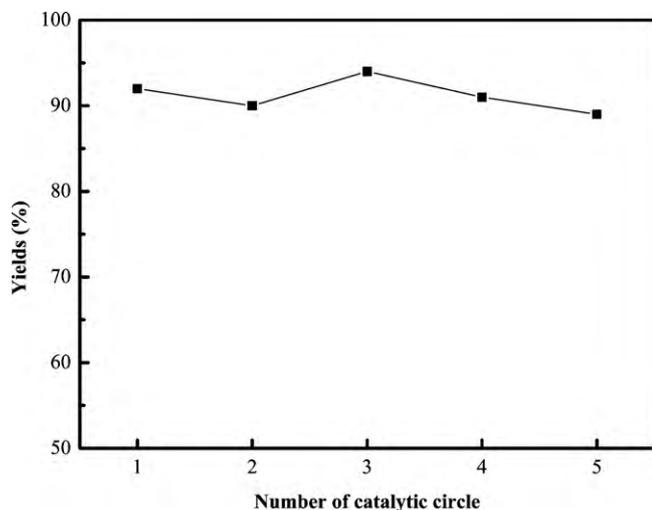


Fig. 5. Recycling of the 0.26 wt% Pd/TiO₂-ads catalyst in the Heck reaction between 4-iodoanisole and methyl acrylate.

runs, respectively (Fig. 5). This demonstrates the 0.26 wt% Pd/TiO₂-ads sample obtained by the pH-controlled adsorption method is a reusable catalyst.

It should be noted that 0.26 wt% Pd/TiO₂-imp catalyst prepared by the conventional wet impregnation method only provided a 27% isolated yield for the Heck reaction of bromobenzene and methyl acrylate under identical experimental conditions. Obviously, the 0.26 wt% Pd/TiO₂-imp catalyst exhibited significantly lower activity than the Pd/TiO₂-ads catalyst due to the conglomeration of particles. It can be seen Pd nanoparticles aggregated to a large particle in contrast with the clear dispersion of 0.26 wt% Pd/TiO₂-ads catalyst by TEM (Fig. 4 and S3). In addition, Heck reaction of bromobenzene and methyl acrylate hardly occurred in the presence of the unsupported fresh PdO or PdCl₂ for 24 h under our reaction conditions even if the amount was increased to 5 mol%. In other words, the 0.26 wt% Pd/TiO₂-ads catalyst prepared by the adsorption method played an important role during the reaction, allowing Heck reaction to easily occur.

4. Conclusions

The Pd/TiO₂-ads catalyst, prepared by a simple pH-controlled adsorption method, is an efficient and stable catalyst for the C–C coupling reaction of aryl halides and alkenes. The catalyst activity is observed to depend on the conditions for its preparation and the content of Pd absorbed on the surface of TiO₂. The 0.26 wt% Pd/TiO₂-ads catalyst exhibits high activity and excellent selectivity and corresponding products are obtained with yields in the range 27–96% at 140 °C. During the reaction, palladium nanoparticles are in situ generated via reduction. TEM images indicate that the nanoparticles are nearly monodisperse in size and stabilized on the surface of TiO₂. After the reaction, the leaching of palladium into the solution is very low by ICP. In addition, the catalyst can be readily recovered and reused several times without significant loss of catalytic activity. Further study to clarify the reaction mechanism and other applications of this catalyst are underway in our group.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.06.004.

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