

A highly efficient heterogeneous catalytic system for Heck reactions with a palladium colloid layer reduced *in situ* in the channel of mesoporous silica materials†

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A new catalyst, Pd–SBA, was prepared by the introduction of an Si–H function into the channel of SBA-15 mesoporous materials resulting in a highly dispersed metal colloid layer on the pore walls of the support material, creating one of the most active heterogeneous catalysts for Heck coupling reactions.

The Pd-catalyzed arylation or vinylation of olefins, universally referred to as the “Heck reaction”, has received increasing attention in the last decade, as it is a selective method to form new C–C bonds in a single operational step.^{1–2} The reaction is appealing because of its tolerance of nearly any solvent and functional group on the substrates, its high selectivity, and its moderate toxicity.^{3–4} The Heck reaction is mostly catalysed by palladium complexes with phosphine ligands in homogeneous solution.^{5–7} It was also shown, however, that heterogeneous Pd catalyst systems, namely stabilized colloidal palladium^{7–10} and supported palladium catalysts,^{11–16} are also active in the reaction. The most recent findings show that even Heck coupling of chloroarenes can be induced by heterogeneous Pd catalysts to give the corresponding vinylarenes at high yields under appropriate reaction conditions.^{15,17} Ying and co-workers reported that mesoporous SiO₂ with highly dispersed Pd could be used as a heterogeneous catalyst in the Heck reaction of *n*-butyl acrylate with a bromoaromatic compound, showing relatively high catalytic activity.¹⁸ Pd was deposited in the porous framework *via* vapor grafting and then reduced by H₂. However, synthesis of such a material needs complicated equipment and the suitable precursors are limited in terms of high volatility and thermal stability. Recently, a facile *in situ* reduction method for the controlled deposition of metals onto the inner surface of silica mesoporous materials was disclosed by our group. It was shown that the treatment of trimethoxysilane allows the immobilization of the Si–H function. This surface hydrosilane function is capable of the *in situ* reduction of metal ions resulting in the deposition of a uniform thin metal colloid layer on the pore channel surface of mesoporous materials. Here we report the synthesis of a thin palladium colloid layer on the pore channel surface of mesoporous silica and its high and repeatable catalytic activity as a heterogeneous catalyst in Heck reactions.

The mesoporous silica SBA-15 was synthesized according to the literature using tri-block poly(ethylene oxide)poly(propylene oxide)poly(ethylene oxide), EO₂₀PO₇₀EO₂₀, as a template under acidic conditions.¹⁹ After functionalization with trimethoxysilane on the pore surface (SBA–H), the mesoporous material was treated with a 0.05 mol l^{–1} Pd(Ac)₂–THF solution, then filtered and dried under vacuum at room temperature giving a grey palladium-containing powder (Pd–SBA).

The as-synthesized Pd–SBA catalyst retained its hexagonally packed porous structure as shown by the small angle XRD pattern; one major peak at about 0.9° together with two additional peaks can be observed, characteristic of the hexagonal mesoporous structure of SBA-15. Palladium metal has major diffraction peaks at 2θ = 40.1° (111) and 46.7° (200), which were not found in the XRD pattern of Pd–SBA (Pd content: 5.0 wt%), indicating that palladium

was highly dispersed in the Pd–SBA. The BET specific surface area of the Pd–SBA sample has only a very limited decrease after Pd incorporation (from 408 to 379 m² g^{–1}). This suggests that the incorporated Pd occupied very limited space and almost all of the nano-pore channels of the host silica remain open. The BJH (Brunauer–Joyner–Halenda) pore size distribution of Pd–SBA had a narrow peak centered at 66.6 Å which was, as expected, slightly smaller than that determined for the SBA-15 starting material (77.5 Å) due to the presence of grafted palladium metal in Pd–SBA. TEM examination shows the hexagonally packed pore structure of Pd–SBA (Fig. 1(a)), with no noticeable palladium clusters. The existence of Pd in the prepared materials can be proved by the simultaneous energy dispersive spectroscopy analysis of X-rays (EDAX), which reveal a Pd composition of about 5 wt% on average. Fig. 1(b) shows the X-ray photo-electron spectrum of Pd–SBA in the Pd 3d_{3/2}, Pd 3d_{5/2} binding energy region with a spin-orbit separation of 5 eV. The Pd 3d_{3/2} peak is centered at 340 eV and the Pd 3d_{5/2} peak at 335 eV; these match well with Pd⁰ 3d_{3/2} and Pd⁰ 3d_{5/2} and no obvious peak for Pd²⁺ was observed. This confirmed that almost all of the Pd²⁺ had been reduced *in situ* to Pd⁰ by Si–H groups on the surface of parent materials.

The Pd–SBA material is applied to catalysis of the Heck carbon–carbon coupling reactions of aryl halides (Scheme 1). The catalytic activity of this material was investigated with styrene and methyl acrylate as the vinylic substrate. The reactions were conveniently carried out in a reactor in air at temperatures of between 120 and 170 °C (Table 1). The yields for the aryl halides with respect to reaction time and amount of catalyst showed that the Pd–SBA catalyst has an excellent activity for Heck carbon–carbon coupling reactions. Investigation into the reaction kinetics of methyl acrylate with 4-bromoacetophenone (Fig. 2) showed a typical initiation period of 5 min required to heat the reaction mixture to the appropriate temperature. Addition of the catalysts to a preheated reaction mixture resulted in instantaneous reactions. Full conversion and a yield of 99% were obtained after only 50 min for the reaction of methyl acrylate and 4-bromoacetophenone with as little

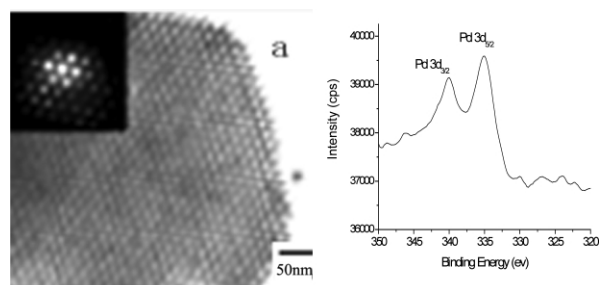
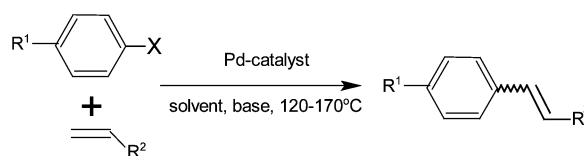


Fig. 1 HRTEM image (a) and XPS spectrum (b) of the Pd–SBA sample.



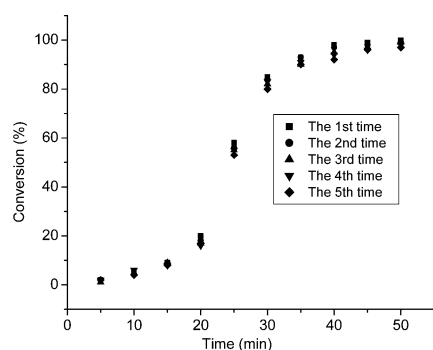
Scheme 1 Heck coupling.

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b4/b404916k/>

Table 1 Heck olefination^a of aryl halide over Pd–SBA catalysts

Vinyl	Aryl halide substrate ^b	Reaction conditions	Conversion (yield) (%) ^{c,d}	Pd (in solution) (ppm)
Styrene	PhI	140 °C; 2 h	100 (88)	0.2
	PhBr	170 °C; 48 h	37 (85)	0.1
	4-BrPhNO ₂	120 °C; 8 h	99 (97)	0.2
	4-BrPhCOCH ₃	120 °C; 45 min	95 (99)	0.2
Methyl acrylate	PhI	140 °C; 2 h	100 (91)	0.3
	PhBr	170 °C; 48 h	50 (94)	0.2
	4-BrPhNO ₂	120 °C; 20 min	100 (98)	0.4
	4-BrPhCOCH ₃	120 °C; 50 min	100 (99)	0.1

^a All reactions were carried out in air with 0.02 mol% Pd–SBA as catalyst. ^b 1.1 equiv of base N(C₂H₅)₃ with respect to aryl halide substrate was added to the reaction mixture. ^c Conversion of reactant was determined by GC-MSD. ^d Yield = (mol of coupling product/mol of reactant converted).

**Fig. 2** Conversion as a function of time for the Heck reaction of 4-BrPhC(O)CH₃ with methyl acrylate at 120 °C with 0.02 mol% catalyst.

as 0.02 mol% catalyst. The elemental analysis showed that there was less than 0.4 ppm Pd in all of the Heck reaction mixtures as determined by ICP. The modified materials showed very high stability against leaching of the active species into the liquid phase than other heterogeneous catalysts^{15,20,21} under the given reaction conditions. This feature is important for a heterogeneous catalyst system.

The Pd–SBA catalyst recycling studies were also performed using the reaction of methyl acrylate with 4-bromoacetophenone, by recycling and then using the material under the same conditions. Before reuse, the solid was separated from the reaction medium by filtration, washed with dichloromethane and finally dried at 40 °C. The results are shown in Fig. 2; the reaction conversion shows that the immobilized catalyst can be repeatedly used without any apparent decrease in its catalytic activity and the selectivity is also kept at the same level after regeneration.

Compared to other heterogeneous Pd catalysts,¹⁸ Pd–SBA shows relatively high catalytic activity in Heck reactions. It only needs about one fifth the amount of catalyst to reach the same conversion under the same reaction conditions. We attribute this to the high

dispersion of Pd in the form of an ultra-thin colloid layer on the surface and in the channel of the host.

An advantage of the Pd–SBA catalyst was that its synthesis was very simple. The palladium metal could be almost fully recovered, and the recovered Pd–SBA catalyst showed almost the same catalytic activity as the first time. The Pd–SBA system is a simple and efficient heterogeneous catalyst for Heck reactions.

In conclusion, a new heterogeneous catalyst system Pd–SBA has been successfully prepared by a selective and *in situ* reduction method. Mesoporous SBA-15 was used as the support since its well-defined, large pore opening provided easy access for large substrate molecules. The introduction of a hydrosilane function on the pore channel surface resulted in a highly dispersed metal colloid layer on the pore walls of the support material, providing excellent catalytic activity for Heck carbon–carbon coupling reactions in air.

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