Palladium-grafted mesoporous MCM-41 material as heterogeneous catalyst for Heck reactions

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Palladium grafted mesoporous MCM-41 materials, prepared by vapor grafting, show remarkable activity in Heck carbon–carbon coupling reactions.

Current research focuses on the synthesis and application of modified mesoporous MCM-41 materials[1,2] that have an active species attached to the framework *via* host–guest interactions, creating discrete and uniform catalyst sites on the inner walls of the porous systems. Herein we report the synthesis of palladium-grafted mesoporous materials, designated Pd-TMS11, and their application as heterogeneous catalysts in Heck reactions. Palladium catalyzed carbon–carbon bond formation, the Heck reaction,[3] represents one of the most versatile tools in modern synthetic chemistry and has great potential for industrial applications. Although recent advances in homogeneous[4] and heterogeneous[5] Heck catalysis have attracted considerable attention, the properties and activities of the existing catalysts have, as yet, limited industrial application. Here we report the synthesis of a highly active heterogeneous palladium catalyst, Pd-TMS11, that exhibits excellent activity towards activated and non-activated haloarene substrates.

Palladium-grafted mesoporous material (Pd-TMS11) is synthesized by vapor deposition of a volatile palladium complex onto the inside walls of the porous framework, followed by reduction. The success of grafting the inside of a porous material with a highly dispersed metal film is strongly dependent on the properties of the volatile complex and the reaction conditions.† To maintain the uniform structure, high surface area and accessibility of the molecular sieves, it is important to minimize the cluster growth inside and outside of the porous material. The concept of vapor grafting enables a uniform distribution of a volatile complex and ensures the discrete deposition of metal fragments throughout the porous structure of the material without cluster formation, giving metal-grafted molecular sieves.

The palladium grafting of the degassed silicate-based MCM-41 material‡ was carried out *via* sublimation of the volatile organometallic complex[6] [Pd(η-C_5H_5)(η^3-C_3H_5)] under vacuum through the porous material. After the palladium complex is deposited onto the inside walls of the pores, the material is reduced under a stream of hydrogen gas, giving an air-stable, black powder.

The prepared catalyst,§ Pd-TMS11, retains its hexagonally-packed porous structure as shown in X-ray diffraction (XRD) pattern. Although the diffraction patterns of Pd-TMS11 and the MCM-41 starting material are almost identical, the peak intensity for Pd-TMS11 is reduced owing to radiation diffusion caused by the grafted palladium metal. The XRD pattern of palladium metal has major diffraction peaks at $2\theta = 40.1°$ (111) and 46.7° (200), which are not found in the XRD pattern of Pd-TMS11, indicating that the palladium metal is highly dispersed in the latter. Further evidence is provided by transmission electron micrograph¶ (TEM) that shows the hexagonally packed porous structure of Pd-TMS11 (Fig. 1), with no noticeable palladium clusters. In addition, scanning transmission electron micrographs (STEM) and energy dispersive analysis by X-ray (EDAX) studies have been conducted on Pd-TMS11 particles, indicating that palladium is uniformly dispersed over the pore surface of the mesoporous support. Elemental analysis of Pd-TMS11 samples shows palladium metal contents of 10–30 mass%, depending on the amount of volatile complex [Pd(η-C_5H_5)(η^3-C_3H_5)] used in the vapor grafting process. The BET surface area of a typical sample of Pd-TMS11 with a palladium content of 19.1 mass% is 750 $m^2\ g^{-1}$. The BJH (Brunauer–Joyner–Halenda) pore size distribution of Pd-TMS11 illustrates a narrow peak centered at 26 Å for the pore diameter which is, as expected, slightly smaller than that determined for the MCM-41 starting material (27.4 Å) owing to the grafted palladium metal. The CO adsorption studies of Pd-TMS11 show metallic surface areas between 120 and 140 $m^2\ g^{-1}$ (Pd metal) with a metal dispersion of more than 30%. In comparison, commercially available Pd/γ-Al_2O_3 (Aldrich) shows a metallic surface area of only 60 $m^2\ g^{-1}$ (Pd metal) with a metal dispersion of 15%.

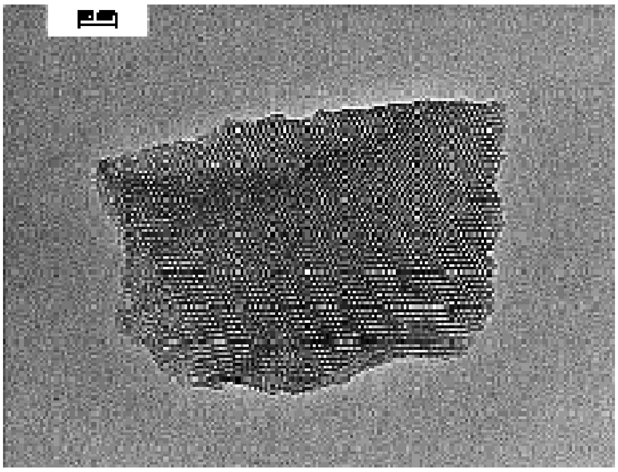
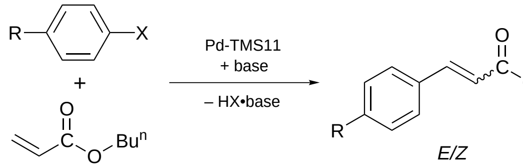


Fig. 1 TEM of Pd-grafted mesoporous catalyst, Pd-TMS11, showing the hexagonal array of 26 Å pores

The Pd-TMS11 materials catalyze the Heck carbon–carbon coupling reaction of aryl halides (Scheme 1). The catalytic activity of these materials was investigated using activated and non-activated aryl halides and butyl acrylate as the vinylic substrate (Table 1). The yields for the activated aryl halides, with respect to reaction time and amount of catalyst, showed that the Pd-TMS11 catalysts have an excellent activity especially in view of other palladium-based heterogeneous systems.** Full conversion and a yield of 99% was obtained after



R	H	H	NO_2	C(=O)Me
X	Cl	Br	Br	Br

Scheme 1

Table 1 Heck alkenation[a] of aryl halides with *n*-butyl acrylate over Pd-TMS11 catalysts

Aryl halide substrate[b]	Amount of catalyst (mol%)	T/°C	Time	% Conversion[c] % (Yield)[d]	E : Z	TON[e]
C_6H_5Cl	0.1	170	32 h	16 (40)	99 : 1	64
C_6H_5Br	0.1	170	48 h	67 (92)	99 : 1	624
4-$BrC_6H_4NO_2$	0.1	120	90 min	100 (99)	99 : 1	1000
4-$BrC_6H_4C(O)CH_3$	0.1	120	25 min	100 (99)	99 : 1	1000
4-$BrC_6H_4C(O)CH_3$	0.02	120	60 min	100 (99)	99 : 1	5000

[a] All reactions are carried out in air. [b] 1.1 equiv. of base NEt_3 with respect to the aryl halide substrate is added to the reaction mixture. [c] Conversion of reactant is determined by gas chromatography. [d] Mol of coupling product (E + Z)/mol reactant converted. [e] TON = mol product/mol catalyst; recycled catalyst showed reduced activity.‖

only 1 h for the reaction of *n*-butyl acrylate and 4-bromoacetophenone using as little as 0.02 mol% catalyst. The Pd-TMS11 material therefore provides an extremely simple and efficient Heck catalyst that even rivals some of the best homogeneous catalysts.[7,††] A moderate conversion of non-activated aryl halides was observed, and a conversion of 67% for bromobenzene has been achieved (see Table 1).

The new catalyst system Pd-TMS11, prepared by vapor grafting, has successfully been used in carbon–carbon coupling reactions. Remarkable activity, easy accessibility and exceptional stability of the described material provides an excellent example for a new generation of heterogeneous Heck catalysts.

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Footnotes and References

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† MCM-41 material was degassed at 60 °C under reduced pressure to prevent decomposition of the palladium complex due to air oxidation or hydrolysis *via* surface adsorbed water. To achieve a uniformly grafted Pd-TMS11 it is necessary that the surface of the MCM-41 be water-free and only consist of surface bound oxo and hydroxo groups.

‡ Modified synthesis of mesoporous MCM-41. Hexadecyltrimethylammonium bromide (15.9 g, 44.9 mmol) was dissolved in H_2O (1.2 l) and treated with sodium silicate (14% NaOH/27% SiO_2) and 1 g (3.14 mmol) $Nb(OEt)_5$ in H_2O (0.4 l) to give a white precipitate.‡‡ The pH value of the mixture was adjusted to pH = 11.5 using sulfuric acid (30%). The gel was aged at room temp. for 12 h before it was heated in pressure tubes to 100 °C for 7 d. The supernatant of the aged gel was decanted off and the resulting white residue washed with H_2O (1 l) and EtOH (1 l). The isolated solid was dried in air at room temp. for 12 h before the material was calcined at 560 °C for 6 h giving MCM-41 with a hexagonally-packed cylindrical mesoporous structure.

§ Synthesis of palladium-grafted mesoporous material (Pd-TMS11). MCM-41 (0.5 g) [XRD (100) 39.9 Å, (110) 22.5 Å, (200) 19.6 Å, (210) 14.8 Å; BET surface area of 997 $m^2 g^{-1}$, BJH adsorption pore size of 27.4 Å] was degassed at 600 °C under reduced pressure (10^{-2} Torr) for 6 h. The resulting material was loaded into a short path frit and contained with glass wool under an inert gas atmosphere. A small round-bottom flask was filled with the red complex $[Pd(\eta^3\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ (0.25 g, 1.2 mmol) and connected to a prepared frit that was further attached to a condensation bridge with a round-bottom flask. The apparatus was evacuated, and a constant pressure (10^{-2} Torr) was maintained by cooling the empty round-bottom flask to −196 °C. The small round-bottom flask containing the volatile palladium complex and the loaded frit were heated to 120 °C (ramp 1 °C min^{-1}) using an oil bath. During the heating process, the white MCM-41 starting material turned black and the excess volatile organometallic complex was condensed into the cooled round-bottom flask. The resulting solid was reduced under a stream of hydrogen (50 ml min^{-1}) at 300 °C, giving a black powder designated Pd-TMS11 [XRD (100) 39.6 Å, (110) 22.4 Å, (200) 19.4 Å].

¶ An average of 50 particles per sample was investigated *via* TEM. No palladium clusters were observed on the as-synthesized Pd-TMS11 material, even at high magnification. TEM investigation of used Pd-TMS11 catalyst showed the formation of palladium clusters (*ca.* 50 Å diameter).

‖ Catalyst deactivation is noted in the form of palladium metal agglomeration, fracturing of the MCM-41 support material and coking of the catalyst surface. Pd-TMS11 recovered from the reaction of *n*-butyl acrylate and 1-bromo-4-nitrobenzene showed reduced activity in the second and third catalysis cycles under identical condition. The total lifetime of the catalyst is *ca.* 3000 TON for the latter reaction.

** Control experiments using commercially available Pd/Al_2O_3, Pd/SiO_2 and Pd/carbon (all containing *ca.* 10 mass% palladium) were conducted giving TONs which were 60% lower than those obtained for Pd-TMS11 with respect to activated aryl substrates. No activity was observed for non-activated aryl substrates in commercial supported catalysts.

†† Reaction between bromobenzene and *n*-butyl acrylate using homogeneous catalysts showed a TON of 96. In comparison, a TON of 624 was obtained for Pd-TMS11 at 170 °C in the same reaction. Unlike the existing homogeneous catalysts, our Pd-TMS11 is not air-sensitive and can be easily recovered by filtration after usage.

‡‡ The prepared MCM-41 had a niobium content of 1.5 mass% which contributed to the larger wall thickness of the material (18 Å). The dopant had no effect on the catalysis results.

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