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Introduction

Synthesis of a recyclable and efficient Pd(II) 4-(2pyridyl)-1,2,3-triazole complex over a solid periodic mesoporous organosilica support by "click reactions" for the Stille coupling reaction[†]

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A highly efficient, reusable B-PMO-TZ-Pd(II) catalyst was synthesized by anchoring 4-(2-pyridyl)-4-(2pyridyl)-1,2,3-triazole ligand over the surface of an organo-functionalized benzene support containing periodic mesoporous organosilica (B-PMO) via "click reaction" and the subsequent complexation with PdCl₂. B-PMO materials with uniform hexagonal arrangements were prepared using C₁₆ alkyl trimethyl ammonium bromide [CTAB] surfactant under basic conditions. The physiochemical properties of the functionalised catalyst were analysed by elemental analysis, ICP-OES, XRD, N₂ sorption, TGA & DTA, solid state 13 C, 29 Si NMR spectra, FT-IR, XPS, UV-vis, SEM and TEM. XRD and N₂ sorption revealed the morphological and textural properties of the synthesized catalyst, confirming that ordered mesoporous channel structure was retained even after the multistep synthetic procedure. The (100), (110) and (200) reflections in B-PMO are evidence of its good structural stability and the existence of long range order. The TGA-DTA results reveal that the synthesized catalyst B-PMO-TZ-Pd(II) was thermally stable, even at high temperature. The organic moieties anchored over the surface of B-PMO were demonstrated by solid state ¹³C NMR and FT-IR spectroscopy. Solid state ²⁹Si NMR spectroscopy provides information about the degree of functionalization of the surface silanol group. The electronic environment and oxidation state of Pd in B-PMO-TZ-Pd(II) were monitored by XPS and UV-visible techniques. Moreover, the morphologies and topographic information of the synthesized B-PMO-TZ-Pd(II) catalyst were confirmed by SEM and TEM analyses. The catalytic properties of the catalyst for the Stille coupling reaction were screened, and higher catalytic activities with high TONs were observed. The anchored solid B-PMO-TZ-Pd(II) catalyst can be recycled efficiently and reused several (four) times without a major loss in reactivity.

Since the discovery of silica-based mesoporous materials, extensive research has been devoted to the synthesis of siliceous and non-siliceous mesoporous materials.¹ Furthermore, a new class of organic–inorganic hybrid mesoporous materials integrating organic groups in the wall channel has been reported; in this new class of materials, the organic molecules reside on the pore surfaces, incorporating organic groups (like ethane, ethene, benzene, biphenyl, *etc.*) into the framework as molecularly bridged ligands.² These unique hybrid materials are known as periodic mesoporous organosilicas (PMO) and are obtained by the hydrolysis and condensation reactions of sil-sesquioxane precursors in the presence of surfactant species. A

wide variety of organo-bridged hybrid mesoporous materials are prepared by choosing a suitable organo siloxane precursor, $(R_0O)_3$ -SiRSi $(OR_0)_3$, where $R = -(CH_2)x^-$, $-C_6H_4^-$, or $-CH \equiv CH_-$. The nature of the organic groups in the hybrid materials controls properties including ion exchange capacity and dielectric constant as well as mechanical properties such as surface hydrophobicity and hydrothermal stability.³ The introduction of organic functionalities into the silica framework modifies the physical and chemical properties of the mesoporous materials, while their inorganic features make them more thermally and structurally stable. In addition, the nature of the organic groups integrated inside the frame wall channels of the mesoporous materials can change the nature of the surfactant–silicate interactions and thereby the final structure of the developed materials.⁴

The sustained development of homogeneous catalysts for fine chemical production has led to attempts to heterogenize these catalysts. At present, several methods for the heterogenization of homogeneous catalysts have been explored.⁵ The

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immobilization of metal complexes onto the surfaces of solid supports is highly desirable in the development of reusable catalysts. Recently, the Cu(1)-catalysed azide-alkyne "click chemistry" reaction has received considerable attention due to its simplicity, mild reaction conditions, quantitative conversions and high tolerance of functional groups; this method has been shown to be one of the best tools for covalent attachment between appropriately functionalized molecules and solid supports via 1,2,3-triazole linkages.6 The 1,3-dipolar cycloaddition reactions between organic azides and terminal alkynes were first systematically studied by "Huisgen" several decades ago.7 These reactions demonstrate high regioselectivity to give 1,4-linked triazoles [click triazole] with excellent yields, high atom efficiencies and low by-products. Since the discovery of the click reaction, it has been applied in diverse areas of chemistry such as dendrimers and polymers, drug discovery, materials science and bioconjugation.8 Triazole ligands have the potential to act as nitrogen-donor ligands since they have long been known to coordinate with a variety of transition metals.9 The click method provides an extremely convenient route for the synthesis of (2-pyridyl)-substituted 1,2,3-triazoles, which could be potentially used as 2,2'-bipyridine analogues.10

The palladium-catalysed cross-coupling reactions of aryl halides or halide equivalents with various nucleophiles have been shown to be a highly effective and practical method for the formation of C–C bonds. These coupling reactions make use of a variety of trans-metalating agents such as organoboron,¹¹ organomagnesium,¹² organosilicon,¹³ organostannane¹⁴ and organozinc reagents.¹⁵ Among these, the Stille reaction involves the coupling of an organotin compound with an sp²-hybridized organic halide catalysed by palladium. The popularity of the Stille reaction is typically attributed to the stability in air and functional group tolerance of stannanes as well as their chemoselectivity and broad scope in terms of reaction. This transformation has become a useful synthetic tool for C–C bond formation and can also be extended to numerous organic electrophiles.^{16,17}

Accordingly, in this report, we graft Pd complexes of 4-(2pyridyl)-1,2,3-triazole, a type of "click reaction" product, and its derivatives into B-PMO phases and investigate their catalytic properties in the Stille C–C coupling reaction. The immediate goals of our study were (i) to evaluate the heterogenization method of the 4-(2-pyridyl)-1,2,3-triazole Pd(π) complex on the organo-hybrid mesoporous B-PMO support, (ii) to characterize the heterogenized B-PMO-TZ-Pd(π) by various physiochemical techniques, (iii) to measure the catalytic properties of the complexes on the Stille C–C coupling reaction, and (iv) to determine the stabilities of the catalysts as well as their recycling properties.

Results and discussion

The hybrid mesoporous catalyst B-PMO-TZ-Pd (π) was obtained by the procedure outlined in Scheme 1. First, 3-chloropropyltrimethoxy silane was converted into 3-azidopropyltrimethoxy silane followed by the surface modification of benzene containing periodic mesoporous organosilica (B-PMO) with 3-azidopropyltrimethoxy silane using the post grafting method (Scheme 1A and B).¹⁸ Azide-functionalized hybrid mesoporous benzene-PMO (B-PMO-N₃) was reacted with 2-ethynylpyridine *via* the "click method" to give the 4-(2-pyridyl)-1,2,3-triazole complex, which was further metalated by PdCl₂.¹⁹ The catalytic properties of the synthesised B-PMO-TZ-Pd(II) were screened in the Stille C–C coupling reaction. The synthesized materials were systematically characterised by nitrogen sorption, cross polarization magic angle spinning (CP MAS) NMR and infrared spectroscopies, elemental analysis, and thermogravimetric and differential thermogravimetric (TGA-DTA) analyses to gain complete structural and compositional information.

The small-angle X-ray diffraction (XRD) patterns of the (a) assynthesized B-PMO, (b) surfactant-extracted B-PMO, (c) B-PMO-N₃ and (d) B-PMO-TZ-Pd(II) are shown in Fig. 1. The assynthesized B-PMO sample exhibits an intense peak at a 2θ value of 2.1 and one broad peak at a 2θ value of 4.2. After solvent extraction of as-synthesized B-PMO, the peaks were well resolved, and an increase in peak intensity was observed; this clearly demonstrates the removal of surfactant molecules from the meso-channels of the B-PMO. Three well-resolved peaks were observed and indexed as the (100), (110), and (200) reflections of p6mm hexagonal symmetry.20 In the case of 3-azidopropyltrimethoxysilane (3-Az-PTMS)-immobilized B-PMO, B-PMO-N₃ and B-PMO-TZ-Pd(II) (Fig. 1c and d), the twodimensional hexagonal pore structures are preserved. However, a continuous decrease in peak intensity was observed after each modification. This decrease in peak intensity implies that the azide modification along with the Pd complex immobilization might disturb the order of the mesoporous structure to a certain degree.

The removal of surfactant groups from the pore channels of the hybrid materials, the presence of benzene fragments in the framework, and further modification via triazole ligand (click reaction) on the mesoporous framework were analysed by FT-IR. Fig. 2a-d shows the infrared spectra of the as-synthesized B-PMO, surfactant-extracted B-PMO, B-PMO-N₃, and B-PMO-TZ-Pd(II). In the as-synthesized B-PMO, strong bands are present at 2921, 2851 and 1471 cm⁻¹; the first two bands correspond to the C-H stretching vibration of the surfactant C₁₆-TMABr. The band at 1471 cm^{-1} is due to the C-H bending vibration. The absence of peaks at 2921 cm⁻¹ and 2851 cm⁻¹ in surfactantextracted B-PMO (Fig. 2b) suggests the complete removal of the template during the solvent extraction process.²¹ The presence of the aromatic C-H stretching vibration at 3000 and 3064 cm⁻¹ in all samples suggests the retention of organic fragments $(-C_6H_4-)$ in the framework positions (BTEB). The spectra of all four samples show strong bands at 812 and 690 cm⁻¹, corresponding to aromatic C–H bending, along with at 1656 cm^{-1} , corresponding to the aromatic C=C bending of 1,2-bis-(triethoxysilyl)benzene (BTEB) fragments. The asymmetric and symmetric stretching vibrations of the Si-O bands, which relate to the presence of residual silanol (Si-OH) groups,22 were observed at 1160 cm⁻¹ and 911 cm⁻¹, respectively. In addition, the presence of intense bands at 1050 cm⁻¹ and at 690 cm⁻¹ assigned to the C-Si aromatic stretching vibrations proves that

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Scheme 1 Schematic diagram of (A) synthesis of 3-azidopropyltrimethoxysilane, (B) functionalization of azide over benzene PMO, (C) B-PMO modification *via* 4-(2-pyridyl)-1,2,3-triazole ligand, and (D) Pd metalation over B-PMO-TZ.





Fig. 1 Small angle XRD patterns of (a) as-synthesized B-PMO, (b) AZP^{-1} surfactant-extracted B-PMO, (c) B-PMO-N₃, and (d) B-PMO-TZ-Pd(II). Inset shows the enlarged image of higher order diffraction.

the organic bridge was not cleaved during solvent extraction or further modification processes (Fig. 2b–d). B-PMO-N₃ shows a sharp absorbance at 2106 cm⁻¹, which is a characteristic

Fig. 2 FT-IR spectrum of (a) as-synthesized B-PMO, (b) surfactant-extracted B-PMO, (c) B-PMO-N_3, (d) B-PMO-TZ-Pd(II), and (e) 3-AZPTMS.

stretching vibration of organic azide (N_3) .²³ The absence of this peak in B-PMO-TZ-Pd(u) demonstrates that the azidopropyl group successfully reacted with 2-ethynylpyridine *via* click reaction.



Fig. 3 Solid state 13 C CP/MAS NMR spectra of (a) as-synthesized B-PMO, (b) surfactant-extracted B-PMO, (c) B-PMO-N₃, and (d) B-PMO-TZ-Pd(II). Inset: B-PMO-TZ-Pd(II).

Fig. 3 shows the ¹³C CP MAS NMR spectra of the (a) assynthesized B-PMO, (b) surfactant-extracted B-PMO, (c) B-PMO-N₃, and (d) B-PMO-TZ-Pd(II). All the samples show an intense peak at 135 ppm along with sidebands (denoted with stars) corresponding to the framework benzene carbon atom of the BTEB precursor. In addition, the appearance of intense peaks at 32 and 67 ppm in as-synthesized B-PMO spectrum (Fig. 3a) correspond to the carbon atoms of surfactant molecules. These peaks are absent in the ¹³C NMR spectrum of the surfactant-extracted B-PMO (Fig. 3b), indicating that the surfactant groups were removed from the pores of the hybrid sample during the ethanol extraction procedures.²² In the B-PMO-N₃ spectrum, three peaks at 12, 24, and 56 ppm were observed corresponding to the carbon (C1) attached to Si, the middle carbon (C_2) and the carbon (C_3) attached to the azide (N_3) , respectively.²³ The appearance of smaller peaks at 125, 136, 149 and 166 ppm clearly demonstrate the functionalization of the 4-(2-pyridyl)-1,2,3-triazole Pd(II) complex on B-PMO. These NMR results demonstrate the proper functionalisation of the 4-(2-pyridyl)-1,2,3-traizole Pd(II) complex on the mesoporous B-PMO.

Solid state ²⁹Si CP/MAS NMR spectra of the (a) as-synthesized B-PMO, (b) surfactant-extracted B-PMO, (c) B-PMO-N₃, and (d) B-PMO-TZ-Pd(\mathfrak{n}) are shown in Fig. 4a–d. The spectrum of the surfactant-extracted B-PMO sample shows intense peaks at -57ppm, corresponding to T² sites [R–Si–(OSi)₂–OH], and -68 ppm, corresponding to T³ sites [R–Si–(OSi)₃]. The absence of Q units [Q_nSi(OSi)_n(OH)_{4–n}] below -100 ppm confirms that there is negligible hydrolytic Si–C bond cleavage, and that the bridgebonded organic group is intact in the silica framework under the synthetic conditions. After solvent extraction and modification, only Tⁿ sites are present in all the prepared samples, indicating that the solvent extraction treatments removed the organic surfactant groups from the wall positions.²⁴ The organosilica samples (Fig. 4b–d) also show a decreased percentage of T² sites after grafting with the 4-(2-pyridyl)-1,2,3-triazole Pd(\mathfrak{n})



Fig. 4 Solid state ^{29}Si CP/MAS NMR spectra of (a) as-synthesized B-PMO, (b) surfactant-extracted B-PMO, (c) B-PMO-N_3, and (d) B-PMO-TZ-Pd(1).

complex; a corresponding increase in the T³ sites, which show more intense anchoring of the 3-azidopropyltrimethoxysilane (3-Az-PTMS), in addition to a small T¹ peak are also visible. The silicon resonances of partially condensed T² [(SiO)₂(OH)–Si–C] and complete condensed T³ [(SiO)₃Si–C] sites are highly intense in comparison to the T¹ [(SiO)(OH)₂–Si–C] site. This indicates the presence of organic moieties inside the framework and a high degree of condensation of the silanol groups.

Thermal analyses (TGA and DTA) of the (a) as-synthesized B-PMO, (b) surfactant-extracted B-PMO, (c) B-PMO-TZ, and (d) B-PMO-TZ-Pd(II) were carried out in air to investigate the thermal stabilities of the synthesized hybrid materials; the results are shown in Fig. 5. TGA plots of all the synthesized and modified B-PMO samples show approximately 5% weight loss below 120 °C caused by the desorption of physisorbed water molecules. The ~12 weight% loss observed between 200 °C and 370 °C for the as-synthesized B-PMO corresponds to the removal of trapped surfactant within closed pores [Fig. 5A(a) and B(a)]. In contrast, the absence of TGA and DTA weight losses in the surfactant-extracted B-PMO between 200 °C and 370 °C [Fig. 5A(b) and B(b)] indicates the complete removal of surfactant from B-PMO. The matrix decomposition, *i.e.*, the loss of benzene [1,2-



Fig. 5 (A) TGA and (B) DTA plots of (a) as-synthesized B-PMO, (b) surfactant-extracted B-PMO, (c) B-PMO-TZ, and (d) B-PMO-TZ-Pd(II).

bis(triethoxysilyl)benzene (BTEB)] fragments bonded in the mesopore frame wall channels observed in the range of 600–650 °C for all samples (Fig. 5A and B), demonstrates that the present mesoporous host materials (B-PMO) are thermally stable up to a temperature of 600 °C.²⁵ The DTA plot of B-PMO-TZ [Fig. 5B(c)] shows two distinct exothermic peaks between 223–273 °C and 318–338 °C due to the propyltrimethoxysilane linker group and the 1,2,3-triozole ring, respectively, along with the benzene fragment exothermic peak at 611 °C [Fig. 5A(c)]. B-PMO-TZ-Pd(II) also exhibits two broad peaks between 250 °C and 400 °C and between 450 °C and 600 °C; the former weight loss may be due to the decomposition of the 1,2,3-triaozole Pd complex occluded in the mesoporous benzene-PMO, while the latter weight loss might correspond to the decomposition of matrix benzene moieties.

The UV-vis spectra of the (a) as-synthesized B-PMO, (b) surfactant-extracted B-PMO, (c) B-PMO-N₃, (d) B-PMO-TZ, and (e) B-PMO-TZ-Pd(II) are shown in Fig. 6. The spectra of all B-PMO samples show two typical sharp absorption peaks at 220 and 275 nm corresponding to the π - π * interaction between the phenylene groups present in the B-PMO network. After the surfactant extraction process, an increase in absorption intensity of the 220 and 275 nm peaks was observed in B-PMO, which may be due to an increase in π electron interaction in the phenylene ring without surfactant molecules. In the case of B-PMO-TZ, the π - π * transition between 275 and 288 nm is well matched with the reported value.26 The palladium complex B-PMO-TZ-Pd(II) shows broader absorption bands between 275 and 288 nm (Fig. 6e) than B-PMO-TZ (Fig. 6d). The B-PMO-TZ-Pd(II) shows two broad bands at around 379 nm and 424 nm, which are tentatively assigned to the metal to ligand charge transfer transition (MLCT); according to the literature, these two bands can be assigned to the MLCT and the Pd⁺² d-d transition, respectively.27 The broad absorption at up to 600 nm in the spectrum of B-PMO-TZ-Pd(II) may be due to the strong stabilization of the $PdCl_2$ complex on the modified B-PMO surfaces.

The nitrogen adsorption–desorption results for B-PMO and B-PMO-TZ-Pd(π) along with their corresponding pore size distribution curves are plotted in Fig. 7. The surface area, average pore diameter (D_p) and pore volume (V_p) observed for the B-PMO and B-PMO-TZ-Pd(π) samples are summarized in Table 1. All samples show type-IV adsorption–desorption isotherms with the nitrogen uptake step at $P/P_0 = 0.3-0.4$, according to the IUPAC classification of mesopores.

The total surface area, average pore diameter and pore volume were 796 m² g⁻¹, 38 Å, and 0.49 cm³ g⁻¹, respectively, for B-PMO and 412 cm³ g⁻¹, 33 Å, and 0.21 cm³ g⁻¹, respectively, for B-PMO-TZ-Pd(II). The decrease in the total mesoporous pore volume (58%), surface area (49%) and pore diameter (14%) after metal complex immobilization on the B-PMO surface is indicative of the grafting of complexes inside the channels of mesoporous B-PMO. From Table 1, it is clear that even though silvlation procedures changed the textural properties of the mesoporous material, the decrease is more prominent after complex immobilization since the bulkier organic moieties inside the pore channels occupy a large area of the void space. Due to the anchoring of the 4-(2-pyridyl)-1,2,3-triazole Pd(II) complex, the capillary condensation steps of B-PMO-TZ-Pd(II) result in reduced P/P_0 values. This shift to slightly lower partial pressures, which indicates a possible reduction in pore size and a partial distortion in pore arrangement, is consistent with the XRD results. The inflection position in N₂ sorption is known to depend on the diameter of the mesopores, and the sharpness usually indicates the uniformity of the mesopores due to the capillary condensation of N2 within the mesopores.

The morphology and structural ordering of the hybrid catalysts were investigated by SEM and TEM. The morphologies of the surfactant-extracted B-PMO and B-PMO-TZ-Pd(π) are shown in Fig. 8A and B, respectively. B-PMO shows uniform arrays of



Fig. 6 DRS-UV-visible spectra of (a) as-synthesized B-PMO, (b) surfactant-extracted B-PMO, (c) B-PMO-N₃, (d) B-PMO-TZ, and (e) B-PMO-TZ-Pd(μ).



Fig. 7 Nitrogen adsorption–desorption isotherms and BJH desorption pore size distribution (inset) for (a) B-PMO and (b) B-PMO-TZ-Pd(II).

Sample	N^{a} (wt%)	Loading of Pd^{b} (wt%)		DET outfood atoo		Dono volumo
		Input	Output	$(m^2 g^{-1})$	diameter $(D_{\rm P})$ (Å)	$(V_{\rm p},{\rm cm}^3{\rm g}^{-1})$
B-PMO				796	38	0.49
B-PMO-TZ-Pd(II)	1.5	4	2.2	412	33	0.21

^a Calculated based on the elemental (nitrogen) analysis value. ^b Input is based on the amount of Pd during the synthetic reaction; output is based on ICP-OES analysis.



Fig. 8 SEM images of (A) surfactant-extracted B-PMO and (B) B-PMO-TZ-Pd(μ).

meso-channels and clear molecular-scale periodicity in the SEM images. The images of B-PMO-TZ-Pd(II) demonstrate that the large molecular system is more dense than B-PMO after the anchoring of the 4-(2-pyridyl)-1,2,3-triazole Pd(II) complex over the mesoporous surface.

The transmission electron microscopy (TEM) images of B-PMO and B-PMO-TZ-Pd(II) are shown in Fig. 9A and B, respectively. These images provide structural evidence that the materials organized into ordered arrays of two-dimensional hexagonal mesopores. The highly uniform mesopores are clearly evident from the TEM image of B-PMO (Fig. 9A), and the formation of the uniformly distributed 4-(2-pyridyl)-1,2,3-triazole Pd(II) complex inside the meso-channels is observed in the TEM image of B-PMO-TZ-Pd(II) (dispersed dark spots in Fig. 9B). These results clearly indicate that the mesopores in B-PMO were retained even after repeated treatments to anchor the 4-(2-pyridyl)-1,2,3-triazole Pd(II) complex over B-PMO.





Fig. 9 TEM images of (A) surfactant-extracted B-PMO and (B) B-PMO-TZ-Pd(II).



Fig. 10 XPS spectrum of B-PMO-TZ-Pd(II).

The Stille coupling reaction is an important reaction for the synthesis of unsymmetrical and symmetrical biaryls. One of the reasons for the popularity of the Stille reaction in modern organic synthesis is the fact that triarylorganotin species are readily available, quite stable in the presence of air and moisture, and tolerate many functional groups. These properties are mostly due to the low polarity of the Sn–C bond. The original Stille coupling reaction requires a highly dry organic solvent, an inert atmosphere, prolonged reaction time and a phosphine containing catalyst.^{30,31} The catalytic properties of the synthesized B-PMO-TZ-Pd(π) catalyst were investigated by reacting iodobenzene with phenyltributyltin in dimethylsulfoxide (DMSO) at 120 °C in the presence of the base cesium fluoride

(CsF); a biphenyl yield of 95% along with a turnover number (TON) of 239 were obtained.

To examine the scope of the catalytic properties of the catalyst for the Stille coupling reaction, a variety of aryl halides were reacted with phenyltributyltin in the presence of a catalytic amount of B-PMO-TZ-Pd(π) (30 mg) at 120 °C in the presence of CsF base and DMSO solvent (Table 2). As shown in Table 2, the Stille coupling reaction of phenyltributyltin with various aryl halides proceeds smoothly under mild reaction conditions giving the corresponding coupled products in high yields (75–99%; Table 2, entries 1–10). The reaction of the mono-substituted aryl halides chlorobenzene, bromobenzene and iodobenzene with phenyltributyltin gave biphenyl yields of 35%, 75%, and 99%, respectively, and corresponding TONs of 84.6, 181.4, and 239.4 (Table 2, entries 1, 2, 3). The low reactivity





^{*a*} Reaction conditions: iodobenzene (1 mmol), phenyltributyltin (1.15 mmol), base cesium fluoride (CsF; 3 mmol), DMSO solvent (3 mL), heterogeneous B-PMO-TZ-Pd(II) catalyst (30 mg), temperature 120 °C. Isolated yields (product) were analysed by GCMS and ¹H, ¹³C CP MAS NMR (see ESI). TON (turnover number) = moles of product converted per mole of Pd.

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of chlorides is usually attributed to the strength of the C–Cl bond (bond dissociation energies for Ph–X where X = Cl: 96 kcal mol⁻¹; Br: 81 kcal mol⁻¹; I: 65 kcal mol⁻¹). From Table 2, it is evident that the reactivity of aryl chlorides and bromides with an arylstannane (phenyltributyltin) was lower than that of aryl iodides, requiring comparatively longer reaction times for completion of the reaction.

Furthermore, electron rich and electron poor aryl halides react smoothly with phenyltributyltin in similar reaction conditions. The electron poor aryl halides 4-chloronitrobenzene, 4bromonitrobenzene and 4-iodonitrobenzene reacted with phenyltributyltin to give the coupled product 4-nitrobiphenyl in yields of 95%, 95%, and 99%, respectively, with TON values of 229.7, 229.7, and 239.4, respectively (Table 2, entries 4, 5, 6). Since the first step of the Stille mechanism oxidative addition of an aryl halide to a Pd metal centre results in a Pd(II) transition state, oxidative addition is often the rate-determining step in the catalytic cycle. The relative reactivity of aryl halides towards the Pd metal centre decreases in the order: $I > Br \gg C1$. Aryl halides activated by their proximity to electron withdrawing groups are more reactive in the oxidative addition than those with donating groups, allowing the use of electron deficient halides such as 4chloronitrobenzene in the cross-coupling reaction. Further, aryl iodides are more reactive than bromides and chlorides; the substituent effect in the aryl iodides appeared to be less significant than in the aryl chlorides and bromides.

The electron rich aryl halides show moderate to excellent reactivity (89–99% yield) for the formation of the corresponding products (4-methylbiphenyl, 4-methoxybiphenyl) in the Stille coupling reaction under similar reaction conditions. The reaction of the electron rich para-substituted aryl halides 4-bromotoluene, 4-iodotoluene and 4-bromoanisole with phenyltributyltin afforded 96%, 99%, and 89% yields after 12 h, 5 h and 9 h of reaction time, respectively (Table 2, entries 7, 8, 9). The coupling reaction of chloronaphthalene with phenyltributyltin was investigated under similar reaction conditions, but no desired coupling product was obtained, even after 24 h of reaction time.

Further, the hydrophobic nature of the support along with the hydrothermal stability and well-ordered mesoporous structure of the framework walls of B-PMO makes the PMO support more advantageous than the classical nano-structured silica support. Due to the presence of evenly-distributed organic moieties (benzene) in defined positions and the covalent anchoring of the metal complex, B-PMO-TZ-Pd(π) is robust enough to withstand the harsh conditions of the catalytic reactions.³² It also provides better access for the substrate molecules into the well-defined active sites in the hydrophobic pore channels of the PMO supports. Moreover, the heterogenized B-PMO-TZ-Pd(π) catalyst offers further advantages such as the easy separation of catalyst and product as well as the possible reuse of the catalysts.

Heterogeneity and recycling studies of the catalyst B-PMO-TZ- $\mbox{Pd}(\pi)$

To investigate the recyclability of the optimized catalyst B-PMO-TZ-Pd(π), the Stille coupling of iodobenzene and

phenyltributyltin was carried out in the presence of DMSO (3 mL) at 120 °C, giving a 99% yield of biphenyl within 2 h. Generally, the Stille coupling reaction generates Bu₃SnI precipitates, which may be deposited on the pore walls of BPMO-TZ-Pd(II) and cause a decrease in the catalytic activity. In the present system, the Bu₃SnI did not slow the reaction, presumably due to the short and highly connected channels in the meso-structures of the organosilica B-PMO-TZ-Pd(II) material, which provides good reactant and product transport. After the reaction, the catalyst was recovered by centrifugation, washed with DMSO and then dichloromethane, sonicated in acetone and finally dried under vacuum overnight. The recovered B-PMO-TZ-Pd(II) was re-used for the same reaction, and the same procedure was repeated four times; the catalyst retained a similar level of activity, indicating the stability of the catalyst (Fig. 11). The present study indicates that the catalyst can be recycled a number of times without losing a significant amount of its activity.

To test if metal was leached from the solid catalyst during reaction, a hot filtration test was performed. In this process, the Stille coupling reaction mixture was collected by filtration at the reaction temperature (120 °C) after a reaction time of 1 h, which gave 58% conversions of iodobenzene. The residual activity of the supernatant solution was studied. After filtration of the B-PMO-TZ-Pd(II) catalyst from the reaction mixture at the elevated reaction temperature (120 °C; in order to avoid possible re-coordination or precipitation of soluble palladium upon cooling), the coupling reactions did not proceed further. These hot filtration test results suggest that Pd was not leached from the solid catalyst during the coupling reactions (Fig. S1, ESI†). These results confirm that the palladium catalyst remains on the support, even at elevated temperatures during the reaction.



Fig. 11 Recycling of the B-PMO-TZ-Pd(II) catalyst. Reaction conditions: iodobenzene (1 mmol), phenyltributyltin (1.15 mmol), base (CsF; 3 mmol), DMSO solvent (3 mL), heterogeneous B-PMO-TZ-Pd(II) catalyst (30 mg), temperature 120 °C.

Conclusion

In summary, a highly stable and recyclable B-PMO-TZ-Pd(II) catalyst has been synthesized by anchoring 4-(2-pyridyl)-1,2,3-triazole over the inner surface of organofunctionalized B-PMO and the subsequent complexation with PdCl₂. The physiochemical properties of the functionalized B-PMO-TZ-Pd(II) catalyst were analysed by elemental analysis, ICP-OES, XRD, N2 sorption, TGA & DTA, solid state ¹³C, ²⁹Si NMR, FT-IR, XPS, UV-vis, SEM and TEM. XRD and N₂ sorption analyses revealed the textural properties of the synthesised catalyst and confirmed that the metal complex was firmly attached to the B-PMO support. The (100), (110) and (200) reflections in the small angle XRD patterns of B-PMO provided evidence for the existence of long range order with structural stability. The thermal stabilities of the synthesized B-PMO and B-PMO-TZ-Pd(II) were revealed by TGA-DTA analysis. Solid state ¹³C NMR and FT-IR spectroscopy confirmed that the organic moieties were anchored over the surface of B-PMO and inside the pore wall. ²⁹Si NMR spectroscopy revealed the presence of only T^n sites, indicating that the solvent extraction treatments had removed the surfactant organic groups from the wall positions. The electronic environment and oxidation state of Pd metal in B-PMO-TZ-Pd(II) were confirmed by XPS and DRS UV-vis techniques. Subsequently, the morphologies of the synthesized catalysts were monitored by SEM and TEM. The catalytic properties of B-PMO-TZ-Pd(II) were screened for the Stille coupling reaction, revealing a high catalytic activity and high TON. The present B-PMO-TZ-Pd(II) catalytic system tolerates a broad range of aryl halide functional groups in the Stille coupling reaction and can be efficiently recycled and reused several (four) times without a major loss in activity.

Experimental

Synthesis of hybrid mesoporous benzene-PMO material

In a typical synthesis for a BTEB-C₁₆TMABr system, 5 g of BTEB was slowly added to a vigorously stirred aqueous solution of C₁₆-TMABr surfactant (3.4 g) in sodium hydroxide (1.8 g). The gel, which had a molar composition of 1 BTEB : 0.67 C16-TMABr: 3.20 NaOH: 450 H2O, was stirred for 20 h at ambient temperature and then allowed to reflux for an additional 48 h at 95 °C. The obtained white precipitate was then collected by vacuum filtration, washed well with deionized water and finally dried at 353 K for 2 h. The surfactant occluded inside the pores of the hybrid materials was removed by stirring the as-synthesized material in an EtOH-HCl mixture at 60 °C for 6 h. The solvent extraction was repeated twice to ensure the complete removal of the surfactant groups. The synthesized material was abbreviated as B-PMO. For the detailed synthetic processes for azide functionalisation over benzene PMO, click chemistry between 2-ethynylpyridine and B-PMO-N₃, metalation over the B-PMO-TZ surface by PdCl₂, see the ESI.[†]

General procedure for Stille coupling reactions

To investigate the catalytic properties of B-PMO-TZ-Pd(π), a Stille coupling reaction was carried out in a 25 mL two neck round bottom flask. In a typical reaction, aryl halide (1 mmol), phenyltributyltin (1.15 mmol), cesium fluoride (CsF; 3 mmol), dimethylsulfoxide (DMSO; 3.5 mL) and B-PMO-TZ-Pd(π) catalyst (30 mg) were stirred under argon at 120 °C. The reaction mixture was analysed by GC at measured time intervals. The products were separated by column chromatography and analysed by GCMS, ¹H, and ¹³C NMR (see ESI[†]).

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