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# Pd nanoparticles dispersed on Zr(IV) organophosphonate: A robust and reusable catalyst for Suzuki-Miyaura cross-coupling reaction

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**Abstract:** A mesoporous zirconium(IV) phosphonate was synthesized by hydrothermal reaction of  $ZrOCI_2.8H_2O$  with a trisphosphonic acid ligand, mesityI-1,3,5-tris(methylenephosphonic acid). Treatment of the mesoporous Zr(IV) phosphonate framework with Pd(OAc)<sub>2</sub> and subsequent reduction produces a nanocomposite where Pd nanoparticles of average size ~ 7-8 nm are found to be homogeneously and abundantly dispersed over the phosphonate framework. The present composite acts as an efficient and reusuable heterogeneous catalyst in Suzuki-Miyaura cross coupling reaction of aryl bromides with aryl boronic acids.

#### Introduction

In recent years, considerable attention has been devoted to metal nanoparticles on account of their diverse applications in catalysis.<sup>[1-5]</sup> Size dependent characteristics and easy surface functionalization of metal nanoparticles fevered their proliferation as selective and efficient catalyst.<sup>[6]</sup> Among the metal nanoparticles, palladium nanoparticles are of particular interest due to their relevance as catalyst in carbon-carbon formation reactions.<sup>[7]</sup> In this regard, palladium nanoparticles supported over heterogeneous materials such as carbon based materials,<sup>[8-10]</sup> polymers,<sup>[11-12]</sup> boron nitride<sup>[13]</sup> and layered double hydroxide <sup>[14]</sup> have gained interest due to significant cost advantage and minimal environmental pollution. It is pertinent to note here that tailoring the stability, activity and selectivity of metal nanoparticle catalyst by chemical modification of the heterogeneous support has remained one of the most pressing challenge in this area.

The ability to tailor the morphology as well as the chemical environment of the voids renders metal organic frameworks (MOFs) as a promising new class of template for hosting nanoparticles. A wide array of metallic nanoparticles e.g. Cu, Ru, Pd, Au, Ag, Pt etc. have been immobilized on several porous MOFs and many of them show excellent catalytic activity in important organic transformations.<sup>[15]</sup> However, degradation of the framework when highly reactive nanoparticles (e.g. Pd) are loaded remains one of the most formidable challenges that need to be addressed before such metals@MOF composites find

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application in industry.

MOFs are generally derived from polycarboxylate based linkers and this can be primarily attributed to the availability of structurally diverse metal carboxylate building blocks.[16] Moreover, carboxylate ion form relatively weak coordination bond with transition metal ions which allows reorganization of the initial polymeric network to result into porous crystalline frameworks. Isolation of crystalline product has greatly assisted in the structural characterization and further advancement of MOFs. However, labile metal-carboxylate linkages also facilitate hydrolytic cleavage of carboxylate based MOFs and therefore integrity of these frameworks have remained a primary concern in their eventual application.[17-21] Phosphonic acids form considerably strong bonds with metal ions as compared to carboxylic acids. Thus, MOFs prepared by using phosphonic acid based linkers offer better framework stability due to the presence of stronger M-O-P bonds. Indeed, high valent metal phosphonate based frameworks have such high stability that they are even inert to very strong base and acid. For example Clearfield and coworkers reported that framework structure of zirconium(IV) phenyl phosphonate remain intact even when treated with fuming sulfuric acid for three days.<sup>[22]</sup> However, the strong M-O-P bonds alleviate formation of poorly ordered layered structure and this prevents accurate structural characterization of high valent metal phosphonates. Moreover, due to the polydentate nature of phosphonate group, the resulting frameworks are comparatively denser and less porous than carboxylate based frameworks.

Interestingly a surfactant assisted sol-gel methodology has been developed recently to assemble mesoporous metal phosphonate frameworks with controlled mesoporosity.<sup>[23]</sup> Herein, surfactant micelle scaffolds act as lyotropic liquid crystalline phase onto which oligomers from the condensation of inorganic/organic precursors condense and undergo polymerization leading to the formation of an ordered mesostructure. A plethora of periodic mesoporous metal phosphonate materials has been assembled so far by using the surfactant-assisted sol-gel method and their pore sizes can be easily tailored by systematic variation of the surfactants.<sup>[24-32]</sup> It is pertinent to note that studies related to the application of metal phosphonate frameworks in catalysis are scarce and this can be partly attributed to the robust nature of the frameworks which make them unsuitable for many catalytic applications.[33-35] Nevertheless, immobilization of catalytically active metallic nanoparticles over metal phosphonates based support offers a unique opportunity to develop robust composites for eventual catalytic application in industry. However, the studies focusing on immobilization of metal nanoparticles on ordered mesoporous metal phosphonate matrices have been largely ignored so far and no metal@mesoporous metal phosphonate composite has been reported till date.[36-38]

During this study a mesoporous Zr(IV) organophosphonate prepared by using a tris-phosphonic acid, mesityl-1,3,5is tris(methylenephosphonic acid) (H<sub>6</sub>L) and following the surfactant assisted sol-gel technique. The resulting mesoporous Zr(IV) phosphonate was employed as a host matrix to support Pd nanoparticles. Both the pristine mesoporous Zr(IV) phosphonate and the Pd@mesoporous Zr(IV) phosphonate composite were characterized by using various analytical, spectroscopic, microscopic and textural analysis. Further, the Pd@mesoporous Zr(IV) phosphonate composite acted as an efficient and reusable catalyst in Suzuki-Miyaura cross coupling reaction between aryl bromides and aryl boronic acids. The synthesis, characterization of the pristine mesoporous Zr(IV) phosphonate and the Pd@mesoporous Zr(IV) phosphonate composite as well as the catalytic application of the composite are described in the present chapter.

## **Results and Discussion**

Hydrothermal reaction of ZrOCl<sub>2</sub>.8H<sub>2</sub>O and H<sub>6</sub>L in presence of cetyltrimethyl ammonium bromide (CTAB) at 130 °C for 3 days and subsequent removal of CTAB by treatment with acidified ethanol produced a mesoporous zirconium phosphonate,  $[Zr_3(L)_2].nH_2O$  (MZrP). Thereafter, impregnation of Pd(OAc)<sub>2</sub> onto the mesoporous framework MZrP followed by reduction led to the isolation of a composite material,  $[Pd_{0.5}Zr_3(L)_2].nH_2O$  (Pd@MZrP) where Pd particles are homogeneously dispersed over the framework (Scheme 1). Both the compounds were characterized by using different spectroscopic, analytical and microscopic techniques such as FT-IR, TGA, powder X-ray diffraction, SEM, TEM, EDX, BET surface area analysis, XPS and solid state NMR.





The FT-IR spectrum of MZrP and Pd@MZrP depicted in Figure S1. Apart from an intense signal observed at 1417 cm<sup>-1</sup> in case of Pd@MZrP, FT-IR spectra of both the compounds show peaks in similar regions which essentially indicate no change in structure of MZrP upon loading of Pd nanoparticles. Intense absorptions at 1031 cm<sup>-1</sup> and 1018 cm<sup>-1</sup> in the FT-IR spectrum of MZrP and Pd@MZrP, respectively, can be easily attributed to P=O and Zr-O-P stretching vibrations. The aromatic C=C stretching vibrations appear as medium intensity signals centered at 1629 cm<sup>-1</sup> and 1643 cm<sup>-1</sup> in the FT-IR spectrum of MZrP and Pd@MZrP, respectively. Absence of any peak within 2850-2930 cm<sup>-1</sup> in both the FT-IR spectra confirms the complete removal of CTAB used during the synthesis of the mesoporous framework. Moreover, broad and intense signals observed near 3400 cm<sup>-1</sup> are attributed to O-H stretching vibration of coordinated and lattice water molecules present in the frameworks.

Thermogravimetric analysis of both the pristine Zr(IV) framework MZrP and its nanocomposite phosphonate Pd@MZrP were performed under N<sub>2</sub> atmosphere to investigate their thermal stabilities (Figure S2). In case of both MZrP and Pd@MZrP, ~14% to 17% weight losses are observed between 28-127 °C and these can be attributed to the loss of surface bound water molecules intercalated within interlayer spacings. On heating beyond 127 °C, the pristine metal phosphonate framework did not show any appreciable weight loss upto 386 °C. However, heating above 386 °C triggers an abrupt weight loss (15%) and this can be attributed to the loss of organic substituents present on the pristine phosphonate framework. On the contrary, the nanocomposite did not show any sharp weight loss on heating above 117 °C. Instead a steady but slow weight loss, which continues even beyond 700 °C is observed. Thus, thermogravimetric analysis clearly reveals the incorporation of Pd nanoparticles greatly enhances the stability of the framework. The interaction of the dispersed Pd nanoparticles with the phosphonate groups of the framework can be possibly attributed to the augmentation of the thermal stability of the composite.

Powder X-ray diffraction patterns of MZrP and Pd@MZrP are depicted in Figure 1. Several broad peaks are observed in powder X-ray diffraction pattern of MZrP and this is characteristic of mesoporous phosphonate frameworks. All the peaks observed in the powder X-ray diffraction pattern of MZrP are also observed in the powder X-ray diffraction pattern of Pd@MZrP albeit with relatively poor intensity. Nevertheless, it clearly establishes that the framework structure of the pristine phosphonate network is intact in the composite Pd@MZrP. Apart from all the peaks corresponding to the phosphonate framework, an intense peak at  $2\theta = 39^{\circ}$  is observed in the powder X-ray diffraction pattern of Pd@MZrP and this can be attributed to the diffraction from 111 plane of Pd(0) nanoparticles.



Figure 1. Powder X-Ray Diffraction spectrum of MZrP (a) and Pd@MZrP (b).

SEM images of MZrP and Pd@MZrP depicted in Figure S4 reveal that the morphology of the pristine phosphonate framework did not change substantially upon incorporation of Pd(0) nanoparticles within the framework. EDX analysis performed along with SEM also confirms the presence of all elements as expected in the prinstine zirconium phosphonate framework as well as in its palladium nanocomposite. TEM images of the composite shows the homogeneous and abundant distribution of Pd(0) particles of average size 7-8 nm over the entire framework (Figure 2).

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Figure 2. TEM images of Pd@MZrP.

The oxidation states of the elements present in MZrP and Pd@MZrP are probed with X-ray photoelectron spectroscopic (XPS) analysis. The broad peak centered at 284.5 eV observed in the C (1s) region of the XPS spectrum of both MZrP and Pd@MZrP can be assigned to aromatic C=C and C-C bonds. Further a broad signal observed at 285.9 eV can be assigned to C-P bonds. Interestingly, the intensity of the peak observed at 285.9 eV diminishes considerably in the composite, Pd@MZrP and a new broad peak centered at 288.7 eV is observed and it can be attributed to the strong interaction of the Pd nanoparticles with the framework (Figure S5).

XPS data of MZrP in 2p region of phosphorus show two broad peaks centered at 134.3 eV and 133.4 eV and these can be easily assigned to  $2p_{1/2}$  and  $2p_{3/2}$  electrons of pentavalent phosphorus. Inclusion of Pd nanoparticles onto the phosphonate framework significantly modify the electronic environment around phosphorus as the peaks corresponding to  $2p_{1/2}$  and  $2p_{3/2}$  electrons of P<sup>5+</sup> are observed at 133.8 eV and 132.7 eV respectively in case of Pd@MZrP (Figure S6).

Additional evidence regarding the strong influence of the Pd nanoparticles on the electronic environement of elements present in the phosphonate framework is acquired from XPS analysis of Zr (3d) region for both MZrP and Pd@MZrP. In case of the pristine zirconium phosphonate framework, peaks corresponding to  $3d_{5/2}$  and  $3d_{3/2}$  electrons of tetravalent zirconium are observed at 183.2 eV and 185.6 eV respectively. However, the characteristic peaks for Zr<sup>4+</sup> (3d<sub>3/2</sub>) and (3d<sub>5/2</sub>) are observed at 182.4 and 184.8 eV respectively in case of the nanocomposite, Pd@MZrP (Figure 3).

XPS analysis of the nanocomposite Pd@MZrP was performed in Pd (3d) region to ascertain the oxidation state of palladium. Two distinct peaks observed at 335.2 and 340.4 eV can be attributed to  $3d_{3/2}$  and  $3d_{5/2}$  electrons of metallic palladium. Apart from that, two additional peaks observed in the Pd(3d) region at 333.1 and 347.2 eV can be assigned to  $3p_{3/2}$ 



Figure 3. XPS spectra of MZrP (a) and Pd@MZrP (b) at Zr (3d) region.

and  $3p_{5/2}$  electrons of tetravalent zirconium present in the framework (Figure 4). It is pertinent to note that peaks for divalent palladium also appear in same region and in order to unambiguously assign these peaks to Zr (3p), we carefully compared the area under the peaks. It may be noted that the area under the peak observed at 347.2 eV is considerably high as compared to peaks observed at 335.2 eV and therefore it is unlikely that they appear from  $3d_{3/2}$  and  $3d_{5/2}$  electrons of divalent palladium. Similarly the area under the peak observed at 340.4 eV is considerably small as compared to the area under the peak observed at 333.1 eV to assign these peaks for  $3d_{3/2}$  and  $3d_{5/2}$  electrons of metallic palladium respectively. Thus, XPS analysis confirms the presence of metallic palladium nanoparticles within the nanocomposite, Pd@MZrP.



Figure 4. XPS spectra of Pd@MZrP at Pd (3d) region.

The textural property of a substance is intimately related to its ability for accommodating guest molecules and therefore BET surface area analysis of the pristine zirconium phosphonate, MZrP was investigated. N<sub>2</sub> adsorption and desorption isotherms of MZrP at 77K shows a type IV N<sub>2</sub> adsorption/desorption isotherm with a hysteresis loop typical of mesoporous frameworks (Figure 5). The sample was desorbed at 300 °C for 3 h. The BJH pore size distribution analysis based on the desorption data reveal the major mean pore diameter as 3.7 nm with two other minor pores of diameters 5.1 nm and 6.4 nm are also prevalent within the mesoporous material. Surface area analysis based on multipoint BET method establish that the pristine zirconium phosphonate framework has a BET surface area 269 m<sup>2</sup>/g and thereby establish the viability of using the

present framework to accommodate metallic nanoparticles over the surface. Micropore volume estimation was performed using t-plot (Figure S7) and micropore surface area was found to be 211.8 m<sup>2</sup>/g while the external surface area is 56.8 m<sup>2</sup>/g. Additionally, the BJH cumilative volume of pores between 2-100 nm diameter was found out to be 0.075 cm<sup>3</sup>/g.



Figure 5. (a)  $N_2$  adsorption/desorption isotherm of MZrP at 77 K (b) BJH pore size distribution pattern of MZrP.

The influence of Pd(0) nanoparticles on the chemical environment of the constituent atoms in the phosphonate framework was investigated by solid state <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy. <sup>13</sup>C NMR spectrum of MZrP showed four well resolved peaks and all of them can be easily assigned to carbon atoms associated to the tris-phosphonate ligand. While peaks at 135.6 and 128.4 ppm can be attributed to two types of aromatic carbon atoms present in the phosphonate ligand, distinct peaks observed at 28.9 and 17.9 ppm correspond to the aliphatic methylene and methyl carbon atoms respectively (Figure S8). <sup>13</sup>C MAS NMR spectrum of the nanpcomposite. Pd@MZrP reveal that the chemical environment of the methyl carbon atom remain largely unaltered upon incorporation of Pd(0) nanoparticles onto the framework as it resonates at 17.7 ppm. However, the peak corresponding to methylene group is slightly downfielded and resonates as a singlet at 30.1 ppm while the two aromatic carbon atoms appear as a broad singlet centered at 132.7 ppm.

Solid state <sup>31</sup>P NMR spectroscopic analysis of MZrP and Pd@MZrP unambiguously establish the strong interaction between the Pd(0) nanoparticles and the zirconium phosphonate framework in the nanocomposite. Solid state <sup>31</sup>P NMR spectra of both the compounds feature only one distinct peak and it reveals the presence of only one type of phosphorus atom in both the cases. Further, the chemical shift of the phosphorus atom present in the pristine phosphonate framework is 12.8 ppm while considerable deshielding is observed in case of the nanocomposite as the <sup>31</sup>P NMR signal appears at 19.9 ppm (Figure S9). Thus, solid state <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy clearly suggest strong interaction between the phosphonate framework and the Pd(0) nanoparticles within the nanocomposite.

# Pd@MZrP catalyzed Suzuki-Miyaura cross coupling reaction

The catalytic efficacy of Pd@MZrP in Suzuki-Miyaura cross coupling reaction between aryl boronic acids and aryl bromides

was investigated (Scheme 2). Initial investigations focused on screening the optimum amount of catalyst, reaction temperature and base for satisfactory conversion. Although substantial conversion was observed at room temperature itself, it was finally established that treatment of reaction mixture at 80 °C in ethanol in presence of 0.15 mol% of Pd catalyst gives the highest yield of cross coupled product (Table 1).



Scheme 2. Suzuki-Miyaura reaction at different conditions with Pd@MZrP as catalyst.

Table 1. Yield at different temperatures to optimize the reaction temperature

SI. No.	Temperature (°C)	Catalyst Amount (mol% of Pd present)	Base	Yield (%)
1	rt	0.10	K <sub>2</sub> CO <sub>3</sub>	50
2	rt	0.10	(Et) <sub>3</sub> N	~0
3	50	0.10	K <sub>2</sub> CO <sub>3</sub>	79
4	80	0.10	K <sub>2</sub> CO <sub>3</sub>	88
5	80	0.07	K <sub>2</sub> CO <sub>3</sub>	81
6	80	0.15	K <sub>2</sub> CO <sub>3</sub>	92
7	80	0.20	K <sub>2</sub> CO <sub>3</sub>	92
8	80	0.10	(Et) <sub>3</sub> N	15
9	80	0.10	NaOH	64
10	80	0.10	Na <sub>3</sub> PO <sub>4</sub>	55
11	80	0.10	Na <sub>2</sub> CO <sub>3</sub>	82
12	80	0.10	NaHCO <sub>3</sub>	35

The catalytic efficacy of Pd@MZrP in Suzuki-Miyaura cross coupling reaction was further investigated by using different phenyl boronic acids and aryl bromides as substrates under the optimum reaction condition. The results of different Pd@MZrP catalyzed cross coupling reactions are summarized in Table 2. It is observed that the presence of electron withdrawing substituent either on the boronic acid or aryl bromide considerably decreased the yield of the cross-coupling product and this is in agreement with the established reaction mechanism of Suzuki-Miyaura cross coupling reaction.

The reusability of Pd@MZrP as a catalyst in Suzuki-Miyaura cross coupling reaction was investigated by using phenyl boronic acid and 4-bromobenzonitrile as substrates. The nanocomposite can be easily recovered quantitatively from the reaction mixture by centrifugation and subsequently decanting the supernatant liquid. The solid catalyst recovered from the reaction mixture was dried in an oven at 100 °C for 2 h to





remove any occluded solvent molecules and then weighed before addition to the next batch of reactants. It was found that Pd@MZrP is an efficient reusable catalyst as the reasonably good yield of the cross-coupling product was obtained upto 5<sup>th</sup> cycle. Observing a stable yield production, the reusability experiments were not continued any further after 5<sup>th</sup> cycle (Figure 6).



Figure 6. Reusability study of catalyst Pd@MZrP for Suzuki coupling reaction.

FT-IR and powder X-ray diffraction analysis of the catalyst recovered after five catalytic cycles was also recorded to examine the structural integrity of Pd@MZrP. All the characteristic peaks observed in FT-IR spectra of the fresh composite are present in the material recovered after fifth catalytic cycles (Figure S10). Similarly, powder X-ray diffraction pattern of the catalyst after fifth cycle does not show any significant difference with that of freshly synthesized catalyst. Moreover, the specific peak obtained for Pd at 20=39° is distinctly seen in the catalyst recovered after fifth cycle which establish the integrity of the composite (Figure S11). The mother liquor isolated on completion of catalytic reactions in each cycle

was further used as catalyst in Suzuki-Miyaura cross coupling reaction. However, no detectable conversion of the substrates were observed in all the cases. Thus, the intigrity of the composite during catalytic reactions was further established by leaching test which ruled out any obvious leaching of immobilized Pd from the composite.

## Conclusions

In summary, a robust mesoporous zirconium phosphonate framework has been prepared by using surfactant assisted solgel method and thereafter palldium nanoparticles are immobilized over the mesoporous framework by impregnation method coupled with subsequent reduction. Detailed analytical, spectroscopic, microscopic and textural studies of the nanocomposite material revealed that palladium nanoparticles of average size 7-8 nm are dispersed homogeneously over the entire zirconium phosphonate framework. Due to the robust nature of the framework as well as strong interaction between the phosphonate groups with the palladium nanoparticles immobilized over the framework, the composite acts as a reusable heterogeneous catalyst in Suzuki-Miyaura cross coupling reaction with reasonably less decrease in efficiency even after repeated use upto 5th times. The mesoporous zirconium phosphonate framework offers a versatile platform to immobilize various reactive metallic nanoparticles primarily due to its robustness and also its ability to anchor different metallic elements through the phosphonate groups. Thus, the present work can be further extended to other metallic nanoparticles which can then be exploited to carry out industrially relevant organic transformations.

## **Experimental Section**

#### Materials and methods

All the chemicals were procured from commercial sources and used as received without any further purification. Solvents were also purchased from commercial sources and were distilled prior to use, adopting common purification techniques. Mesityl-1,3,5-tris(methylenephosphonic acid) was synthesized following a reported procedure.<sup>[39]</sup> Melting points were recorded on a Buchi (M-560) melting point apparatus and reported without any correction. Nicolet Impact I-410 and Perkin Elmer Frontier MIR-FIR FT-IR spectrophotometers were used to obtain Fourier transformed infrared spectra between 400-4000 cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL JNM-ECS400 NMR spectrometer operating at 400 MHz and samples were dissolved in deuterated solvents. Chemical shifts are reported in parts per million downfield of Me<sub>4</sub>Si (TMS) as internal standard. Elemental analyses were performed on a Perkin Elmer Model PR 2400 Series II Elemental Analyzer. ICP-OES analyses were performed on Perkin Elmer Optima 2100DV analyzer. Thermogravimetric analyses were performed on a Shimadzu TGA-50 thermal analyzer. The scanning electron microscopy (SEM) analyses were carried out using a JEOL JSM-6390LV SEM, equipped with an Energy-Dispersive X-ray analyzer. The powder X-ray diffraction patterns were recorded on a Bruker AXS D8 Focus X-ray diffractometer instrument using a nickel-filtered CuKa ( $\lambda$  = 0.15418 nm) radiation source

and scintillation counter detector. Solid state <sup>13</sup>C and <sup>31</sup>P spectra were recorded on a AVANCE III 500WB spectrometer using adamantane (38 ppm) and H<sub>3</sub>PO<sub>4</sub> (0 ppm) as references, respectively. X-Ray photoelectron spectroscopy (XPS) analysis was carried out on a KRATOS Axis Ultra DLD electron spectrometer using an AI K $\alpha$  (1486.6 eV) radiation source. GC-MS was recorded on a Perkin Elmer Clarus 600C Mass Spectrometer. The pore structures were measured by a FEI TECNAI G2 20 S-TWIN transmission electron microscope operated at an accelerating voltage of 200 kV. Nitrogen adsorption/desorption isotherms were obtained by a ASAP 2020 surface area analyzer (Micromeritics).

#### Synthesis of MZrP

Cetyltrimethylammonium bromide (0.18 g, 0.5 mmol) was dissolved in 5 water and stirred for 2 h. Then mesityl-1,3,5mL tris(methylenephosphonic acid) (0.20 g, 0.5 mmol) in 3 mL water was added to the CTAB solution and the resulting solution was stirred for 12 h. ZrOCl<sub>2</sub>·8H<sub>2</sub>O (0.16 g, 0.5 mmol) dissolved in 4 mL water was then added to the above solution under continuous stirring. Soon after the addition of zirconium oxychloride, formation of a cream coloured precipitate was observed. The whole mixture was stirred for another 12 h and finally transferred to a teflon lined stainless steel autoclave, sealed and placed in an electric oven at 403 K for 3 days. After cooling to room temperature, the white product formed was filtered and washed several times with distilled water. To remove the surfactant, the as-synthesized material was heated with 20 mL of acidified ethanol at 333 K and then washed with pure ethanol to remove the remaining acid. The extracted material was dried in vacuum. Yield 0.26 g; Elemental analysis calculated for C24H50O28P6Zr3: C 23.1, H 4.0, P 14.9, Zr 21.9 Found: C 23.5, H 3.9, P 15.0 Zr 21.7. FT-IR (KBr, cm<sup>-1</sup>): 3400 (br), 1629 (m), 1456 (w), 1031 (s), 746 (w), 506 (m); <sup>13</sup>C NMR (δ ppm): 135.6, 128.4, 28.9, 17.9; <sup>31</sup>P NMR (δ ppm): 12.8; XPS (eV): 284.5, 285.9 (C 1s); 134.3, 133.4 (P 2p); 183.2, 185.6 (Zr 3d).

#### Synthesis of Pd@MZrP

Pd(OAc)<sub>2</sub> (0.07 g, 0.34 mmol) was dissolved in 10 mL THF and 0.27 g of compound MZrP was added. The mixture was stirred overnight at room temperature, filtered and the residue was washed several times with THF and the remaining solid was dried under vacuum. Subsequently 0.15 g of the solid was added to 0.04 g of NaBH<sub>4</sub> (1.07 mmol) solution in ethanol at 0 °C and the resulting mixture was stirred for 2 h at room temperature. Later, it was centrifuged, washed with ethanol several times and also with diethylether and finally air dried. Yield 0.16 g; Elemental analysis calculated for C<sub>24</sub>H<sub>54</sub>O<sub>30</sub>P<sub>6</sub>Zr<sub>3</sub>Pd<sub>0.5</sub>: C 21.5, H 4.1, P 13.9, Zr 20.5 Pd 3.9 Found: C 21.2, H 4.2, P 13.8 Zr 20.1, Pd 3.9; FT-IR (KBr, cm<sup>-1</sup>): 3431 (br), 1643 (m), 1417 (s), 1018 (s), 738 (w), 526 (w); <sup>13</sup>C NMR (δ ppm): 132.7, 30.1, 17.7; <sup>31</sup>P NMR (δ ppm): 19.9; XPS (eV): 284.5, 285.9, 288.7 (C 1s); 133.8, 132.7 (P 2p); 182.4, 184.8 (Zr 3d); 333.1, 335.2, 340.4, 347.2 (Pd 3d).

# Typical procedure for Suzuki-Miyaura reaction catalyzed by Pd@MZrP

Aryl boronic acid (0.24 mmol) was dissolved in 6 mL ethanol to which aromatic bromo derivative (0.2 mmol),  $K_2CO_3$  (0.2 mmol) and catalyst Pd@MZrP (0.15 % of Pd) were added. The mixture was refluxed and progress of the reaction was monitored by using TLC. After the reaction was complete, the reaction mixture was filtered and GC-MS of the same was recorded for yield calculation using toluene as the internal standard. The cross coupling products were isolated by column chromatography with 5% ethyl acetate/hexane mixture as eluent and characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR. Yield of all reactions were calculated using GC-MS

after separation of the heterogeneous catalyst from the reaction mixture by filtration. Toluene was used as Internal Standard and IRF value was calculated as-

IRF = (Area ISX Amount SC)/(Amount IS X Area SC)

Where, IS: Internal standard and SC: Substance of consideration.

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**Keywords:** mesoporous framework • zirconium • palladium • catalysis • reusability

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A robust mesoporous Zr(IV) organophosphonate framework is prepared by surfactant assisted sol-gel method and it is used as a versatile scaffold to host Pd nanoparticles of average size 7-8 nm. The Pd nanoparticle impregnated composite acted as a robust, efficient and reusable catalyst in Suzuki-Miyaura cross coupling reaction of aryl bromides with aryl boronic acids.

\*Pd catalyst, Suzuki-Miyaura cross coupling reaction, Zr organophosphonate

## Key Topic\*

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Title

Pd nanoparticles dispersed on Zr(IV) organophosphonate: A robust and reusable catalyst for Suzuki-Miyaura cross-coupling reaction