

Palladium Nanoparticles Encaged in Nitrogen Rich Porous Organic Polymer: Constructing Promising Robust Nanoarchitecture in Catalytic Biofuel Upgrade

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ABSTRACT: Surfactant-free ultrafine Pd nanoparticles (NPs) (2.7-8.2±0.5 nm) based robust nanoarchitecture have been developed by incipient wet impregnation method with subsequent reduction of Pd(II) species encaged into the 1,3,5-triazine functionalized Nitrogen-rich Porous Organic Polymer (POP) employing NaBH₄, HCHO and H₂ reduction routes, respectively. The as prepared Pd-POP materials following three different synthetic methods consist of virtually identical chemical compositions but with different physical and texture properties. Strong Metal-support interaction, nanoconfinement effect of POP and homogeneous distribution of Pd-NPs have been investigated by performing ¹³C CP solid state MAS NMR, FT-IR, XPS, Wide angle Powder XRD, N₂ physisorption, HR-TEM, HAADF-STEM, Energy-dispersive X-ray (EDX) mapping spectroscopic studies. The resulting Pd-POP based materials exhibit highly efficient catalytic performance with superior stability in promoting biomass refining (hydrodeoxygenation of vanillin, a typical compound of ligninderived bio-oil). Outstanding catalytic performance (~98% conversion of vanillin with exclusive selectivity for hydrogenolysis product 2-methoxy-4-methylphenol) has been achieved over the newly designed Pd-POP catalyst under the optimized reaction conditions (140°C, 10 bar H₂ pressure), affording a TOF value of 8.51 h^{-1} and no significant drop in catalytic activity with desired product selectivity has been noticed for the 10th successive catalytic cycles demonstrating excellent stability and reproducibility of this catalyst system. A size- and location-dependent catalytic performance for the Pd-NPs having small size $(1.31\pm0.36 \text{ and } 2.71\pm0.25 \text{ nm})$ has been investigated in vanillin hydrodeoxygenation reaction with our newly designed Pd-POP catalysts. Presence of well-dispersed electron-rich metallic

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Pd sites and highly rigid cross linked amine functionalized POP framework with high surface area is thought to be responsible for the high catalytic activity and improvement in catalyst stability.

KEYWORDS: *Heterogeneous Pd Catalyst* • *Porous Organic Polymer* • *Biomass* • *Biofuel Upgrade* • *Hydrodeoxygenation of Vanillin*

INTRODUCTION: In the past few decades, production of Biofuel and chemical feedstocks from renewable and sustainable biomass has emerged a growing scientific interest as an alternative owing to the continuous depletion on fossil fuel sources.^[1] However the presence of high amounts of oxygen components limited the effective utilization of bio-oils thereby making its' a low calorific value, immiscibility with conventional fuels and instability over time. Therefore, upgradation of bio-oils employing deoxygenation become necessary for their effective utilization.^[2] Lignin which is composed with the ~ 30 wt% of woody biomass has been considered one of the most abundant biosources on earth. Selective modification or deoxygenation of lignin-derived pyrolysis oil has marked serious concerns and challenging task compared with the cellulose-derived pyrolysis oil owing to its exceptionally complicated structure associated with the oxygen-rich subunits derived from phenol, p-coumaryl, coniferyl, and sinapyl alcohols which are naturally attached with ether linkages with no uniform repeating units.^[3] Several kind of approaches have been adopted including dehydration, hydrogenolysis, decarboxylation, decarbonylation and hydrodeoxygenation for bio-oil upgrading to a liquid transportation fuel, among which hydrodeoxygenation (HDO) is considered to be the most effective and feasible strategy for bio-Fuel upgrading.^[4] Recently several research groups have brought into focus the need to find effective strategies for the development of metal nano-structures useful in potential applications in versatile research areas.^[5] Literature survey reports demonstrate that a series of supported noble metal catalysts (like Ru, Pt and Pd) could be employed in successful deoxygenation for a wide range of biomass derived compounds such as phenol, anisole, vanillin and sorbitol.^[6] In this regard, extensive efforts have been focused for the construction of various kind of heterogeneous catalysts to explore hydrodeoxygenation of vanillin (4-hydroxy-3-methoxybenzaldehyde), a typically model component of pyrolysis oil derived from the lignin fraction, with three different types of oxygenated functional groups (aldehyde, ether, and hydroxyl) and its partial solubility in both the organic and aqueous phases just as bio-oil.

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For example, Wang and co-workers have designed novel N-doped carbon-supported Pd catalyst along with the use of some traditional supports such as TiO2, MgO, CeO2 and y-Al₂O₃ and investigated their catalytic performance in the aqueous phase hydrodeoxygenation of vanillin.^[7] They have found that the excellent catalytic activity and selectivity of the desired product could be ascribed to the unique and stable N-doped carbon nanostructure that facilitates homogeneous distribution of Pd nanoparticles with the additional electronic activation of the metal nanoparticles in the reaction medium. Superior catalytic performance for the hydrodeoxygenation of vanillin has been achieved by Xiao and co-workers employing highly active hydrophilic mesoporous sulfonated melamine-formaldehyde resin (MSMF)supported Pd catalyst (Pd/MSMF).^[8] Very recently, Shall *et al.* have developed a Pd@NH₂-UiO-66 catalyst where palladium nanoparticles are encapsulated within amine-functionalized UiO-66 MOF and employed it as a synergic catalyst in hydrodeoxygenation of vanillin.^[9] Shall et al. have also reported synthesis of highly efficient bifunctional catalyst, Pd/SO₃H-MIL-101(Cr) with the facile immobilization of Pd-NP on a mesoporous sulfonic acidfunctionalized metal-organic framework and investigated its catalytic activity in vanillin hydrodeoxygenation reaction.^[10] Pd nanoparticles were stabilized on the N-doped porous carbon derived from metal-organic-framework has been recognized as a potential catalyst (Pd/NPC-ZIF-8) in vanillin hydrodeoxygenation reaction with remarkable catalytic efficiency.^[11] Pd nanoparticle size-and location-dependent catalytic activity and selectivity in HDO of vanillin with Pd-MIL-101 catalyst was reported by Xu and co-workers.^[12] Wang and co-workers have extensively investigated catalytic activity of carbon nanotube supported gold catalyst in bio-oil upgrading using vanillin hydrodeoxygenation reaction.^[6c] However, practical applications of these recent reported supported metal catalysts have been restricted by some obdurate associated problems owing to poor dispersion of nanoparticle on support, weak catalyst-support interactions, uncontrollable growth, reaction monofunctionality and leaching of metal nanoparticles causing an obvious decrease in the catalyst recyclability. Although MOFs with huge surface area and well-defined cavities offer a great opportunity to serve as a promising platform/host for encapsulation of catalytically active particles but their versatile application in heterogeneous catalysis yet remains unexplored due to their moisture sensitivity, physiochemical instability in acids or bases and the labile nature of the metalligand coordination bonds. In contrast with MOF (Metal-Organic-Framework), N-doped carbon, and carbon nanotubes, Porous Organic Polymer (POP) have intrigued incredible degree of awareness as a fascinating candidate for spatial confinement of catalytically active

crystalline metal or metal oxide nanoparticles owing to its interconnected three-dimensional highly rigid symmetric skeletons mechanically stable to heat, moisture, acid and base, designable pore structure, low skeleton density and easily tuneable structural integrity by changing straightforward effective synthesis strategy and selection of monomers.^[13] Very recently, POP-supported metal or metal oxide nanoparticles become very attractive candidate as heterogeneous nanocatalyst in performing hydrogenation,^[14a] oxidation^[14b] and photocatalytic reactions.^[14c, 14d] A certain degree of chemical interaction including coordination and electron transfer between the polymers and metal NPs can surely enhance the catalytic activity and stability of metal NPs thereby evading agglomeration and leaching from the POP networks.



Scheme 1. Schematic illustration showing the synthetic strategy of Pd nanoparticles fabrication into/onto POP and its selective catalysis in biofuel upgrade reaction.

In our previous work, we have accomplished the fruitful synthesis of nitrogen rich Porous Organic Polymer (TRIA) poly-divinylbenzene-co-triallyloxytriazine by nonaqueous radical co-polymerization of 2,4,6-triallyoxy-1,3,5-triazine with the cross-linker divinylbenzene under metal-free and template-free solvothermal conditions.^[14a] Successful

10.1002/cctc.201700186

synthesis of porous organic polymers employing metal-free and template-free radical polymerization under solvothermal conditions has been widely recognised as a promising route for synthesizing functional hierarchically porous organic polymers on the concept of green chemistry and also to avoid metal catalyzed harsh reaction conditions. In the present work, we take advantage of the distinctive features of TRIA-POP including huge surface area with high thermal and mechanical stability that can easily accommodate Pd nanoparticles within the mesoporous cages to develop efficient Pd-catalysts Pd-A, Pd-B and Pd-C, respectively by following three different reduction routes and investigated their catalytic performances in hydrodeoxygenation of vanillin as a model system to explore the hydrogenation and deoxygenation routes of lignin as presented in Scheme 1. Concerning regarding the outstanding thermal and chemical stability of the POP materials, it has been well documented that many of the POPs could be safely exposed in the aggressive media and wet chemical environment without disturbing framework stability and porous structure. For example, the remarkable stability of the resulting POP materials is illustrated by the resistance to high moisture, high acidity, and/or high basicity under catalytic reaction conditions because of their covalent bond-formation chemistry.^[14e] Lin and co-workers have reported the synthesis of highly cross-linked porous polymers by Co₂(CO)₈-mediated trimerization reaction and described their exceptional stability during acidic work up procedure which was most essential to remove the unreacted cobalt species.^[14f] Structural integrity of the organic back-bone unit, porosity, nanostructure, homogeneous distribution of Pd-NPs with the corresponding oxidation state have been investigated by performing ¹³C CP solid state MAS NMR, FT-IR, Wide angle Powder XRD, N₂ physisorption, HR-TEM, HAADF-STEM, Energy-dispersive X-ray (EDX) elemental mapping, XPS spectroscopic studies. Impressive catalytic performance (~98% conversion of vanillin with exclusive selectivity for hydrogenolysis product 2-methoxy-4-methylphenol) has been achieved over the newly designed Pd-POP catalyst with tremendous recyclability after ten recycles in succession, no sign of catalyst deactivation and negligible leaching. An enhancement in the catalytic performance for the Pd-POP catalysts is observed compared with the conventional and reported catalysts under optimized reaction conditions making it a potential catalyst in Biomass refining industry. The enhanced catalytic performance of Pd-POP could be attributed to the intrinsic synergistic effects of Pd-NPs interacting with the nitrogen rich POP with an exceptional porous nanoarchitecture making them electron-rich metallic Pd and hierarchical pores in the interconnected POP network, facilitates hydrogenolysis of the

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intermediate to the targeted product with easy diffusion. To the best of our knowledge, this is the first example for the development of porous organic polymer encapsulated Pd NPs as efficient catalyst with superior stability in promoting biomass refining (hydrodeoxygenation of vanillin, a typical compound of lignin).

Experimental Section:

Materials and methods:

Divinylbenzene, 2, 4, 6-triallyoxy-1, 3, 5-triazine, Azobisisobutyronitrile (AIBN), Pd(OAc)₂, Vanillin, NaBH₄ were procured from Sigma-Aldrich, India and were used respectively without any further modification. Acetone, MeOH, ⁱPrOH and HCHO were supplied by E-Merck, India.

Characterization Techniques:

Powder X-ray diffraction (PXRD) patterns of different samples were recorded with a Bruker D8 Advance X-ray diffractometer operated at a voltage of 40 kV and a current of 40 mA using Ni-filtered Cu K α (λ =0.15406 nm) radiation. High Resolution Transmission electron microscopy (HR-TEM) images were recorded in a JEOL JEM 2010 transmission electron microscope with operating voltage 200 kV equipped with a FEG. Field emission scanning electron microscopic images of samples were obtained using a JEOL JEM 6700 field emission scanning electron microscope (FE-SEM). Nitrogen sorption isotherms were obtained using a Quantachrome Autosorb 1C surface area analyzer at 77 K. Prior to the measurement, the samples were degassed at 393 K for approximately 6 h in high vacuum. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) in the relative pressure (P/P_0) range of 0.01-0.1. The total pore volumes and pore size distribution curves were obtained from the adsorption branches using nonlocal density functional theory (NLDFT) method. FT IR spectra of the samples were recorded using a Nicolet MAGNA-FT IR 750 Spectrometer Series II. Thermogravimetry (TGA) analyses of the all samples were carried out using a TGA Instruments thermal analyzer TA-SDT Q-600 under nitrogen atmosphere with a heating rate of 10°C min⁻¹ from 25 to 600°C. Solid-state ¹³C CP-MAS NMR studies were performed using a Bruker Avance III HD 400 MHz NMR spectrometer. Transmission electron microscope high-annular dark-field scanning (HAADFSTEM) and energy-dispersive X-ray mapping images were obtained with a TECNAI G2 F20 equipped with an EDX detector.X-ray photoelectron spectroscopy (XPS) was performed on an Omicron nanotech operated at 15 kV and 20 mA with a monochromatic Al Ka X-ray source. Quadrupole ion trap Mass Spectrometer equipped with Thermo Accela

LC and Agilent 6890 GC system equipped with a flame ionization detector were used for analysis of catalytic reactions. The loading amounts of Pd were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP-6500DUO, Thermo Fisher Scientific).

Synthesis of Porous Organic Polymer TRIA:

Porous Organic Polymer (TRIA) has been synthesized based on the protocol previously reported by Zhao *et al.*^[14a] In a typical synthetic procedure, divinylbenzene (5.99 mmol, 781 mg), 2, 4, 6-triallyoxy-1, 3, 5-triazine (1.49 mmol, 373 mg) and AIBN (0.152 mmol, 25 mg) were mixed together in acetone (15 mL) and the resulting mixture was stirred at room temperature under N₂ atmosphere for about 6 h. After that, the reaction mixture was solvothermally treated in a teflon lined stainless steel autoclave at 120°C under static condition for 24 h. After cooling, the resulting white color solid material TRIA was isolated washed with acetone followed by methanol and dried in air.

Synthesis of Pd-A:

Typically, 400 mg TRIA polymer was suspended in MeOH (100 mL) and the mixture was sonicated for 30 minutes until it become homogeneous. With constant vigorous stirring 40 mg of Pd(OAc)₂ in 10 mL of MeOH solution was added dropwise over a period of 15 min. Then the resulting reaction mixture was continuously stirred at room temperature for another 15 h. The as-obtained brown colour Pd(II)-POP composite was isolated from the reaction mixture by centrifugation and washed with MeOH for several times. After that the brown solid was re-dispersed in 100 mL water by stirring at room temperature for 2 h. A freshly prepared 1(M) NaBH₄ (2 mL) solution was subsequently added and stirred for another 15 minutes. The black colour solid powder was isolated and designated as Pd-A.

Synthesis of Pd-B:

The brown colour Pd(II)-POP composite was synthesized following the same procedure as described above. After that the brown color solid was re-dispersed in 100 mL water with addition of 0.5 mL formalin (37 wt%) solution and heated the reaction mixture at 80°C for 3h. The mixture was allowed to cool at room temperature and the black colour solid was recovered with careful centrifugation followed by washing with acetone and methanol which was designated as Pd-**B**.

Synthesis of Pd-C:

For the synthesis of Pd-C material the as-synthesized brown colour solid was subjected for heat treatment in a stream of H_2/N_2 (10% H_2 , 100 mL/min) at 200°C for 4 h. The black colour solid was isolated and designated as Pd-C.

Catalytic Hydrodeoxygenation (HDO) of Vanillin:

The catalytic hydrodeoxygenation (HDO) of vanillin was performed in a stainless steel reactor inbuilt with a pressure gauge setup. In a typical procedure under, vanillin (100 mg, 0.657 mmol), Pd-POP catalyst (20 mg, 0.014 wt% of Pd) and isopropanol (30 mL) were charged into the reactor. The reactor was evacuated using a vacuum pump for 15 min at room temperature to remove dissolved O_2 or air and then pressurized with H_2 at a desired pressure with continuous purging by hydrogen gas. The temperature of the autoclave was fixed at 140°C for the desired reaction time with continuous stirring at a speed of 800 rpm. After the reaction, the autoclave was cooled at room temperature and catalyst was separated from the reaction mixture by centrifugation prior to being analyzed by GC. Quantitative analysis for the isolated liquid reaction mixture was performed using dodecane as an internal standard followed by comparison with known standards with a standard deviation less than 2%. Agilent 6980 Gas chromatograph equipped with a flame ionization detector and an SE-54 capillary column (30 m×0.32 mm×1.0 µm) with a stationary phase based on poly(methylphenylsiloxane) has been utilized for the analysis and quantification of the reaction products.

Recycling Test: In a typical recycling experiment of hydrodeoxygenation (HDO) of vanillin with palladium nanoparticles supported POP catalyst, a mixture of vanillin (500 mg, 3.375 mmol), Pd-POP catalyst (100 mg, 0.07 wt% of Pd) and isopropanol (150 mL) was heated to stir at 140°C in a 200 mL dry stainless steel reactor pressurised with hydrogen gas at 10 bar for 15 h. After the reaction, the catalyst was recovered from the reaction mixture by centrifugation, washed with methanol several times followed by acetone, finally dried overnight in an oven at 80°C and then directly used for the next cycle reaction in succession. No any additional specific approach including heat treatment and addition of acid or base is necessary for the reactivation and regeneration of our catalyst.

Hot filtration test: We have conducted hot filtration test in order to establish that our catalyst is unambiguously heterogeneous in nature and no considerable leaching of the catalytic active sites took place into the solution. Typically, 50 mL dry stainless steel reactor pressurised with hydrogen gas at 10 bar was charged with a mixture of vanillin (100 mg, 0.657 mmol), Pd-C catalyst (20 mg) and isopropanol (30 mL) and heated at 140°C. After 6 h

the catalyst was removed from the hot reaction mixture by centrifugation and mixture was examined with GC analysis which provided 54.6% conversion of vanillin. Then we have performed the catalytic reaction running the filtrate with same reaction mixture under stainless steel reactor with identical conditions for further 8 h. After 15 h, no noticeable increase in the vanillin conversion beyond 55% was attained as determined by GC analysis. This investigation definitely illustrates that the palladium nanoparticles were strongly encapsulated with the highly rigid porous organic framework making the system heterogeneous in nature with no evident of metal leaching in the solution as confirmed by AAS analysis measurement of the hot filtrate solution.

Hg(0) poisoning test: In order to examine active catalytic Pd-species is likely to be heterogeneous in nature, a standard Hg-poisoning test was conducted for the successful suppression of the catalytic reaction. Two sets of reactions for hydrodeoxygenation of vanillin were carried charging the stainless steel reactor with the reaction mixtures of vanillin (100 mg, 0.657 mmol), Pd-C catalyst (20 mg) and isopropanol (30 mL), one of them is considered as a control experiment. Vanillin conversions for both set of reactions to 2-methoxy-4-methylphenol were analysed at 140 °C after 6 h by GC-FID. At that time, conversions of 54.6% and 55.3% have been attained for both the reactions, respectively. Then, elemental mercury (100 mg) was introduced to one of the reactor system after 6 h and both reactions were continued for about 18 h. After 18 h, it was discovered that the catalytic reactor system containing Hg furnished only 57.9% vanillin conversion. But on the other hand we have achieved 96.9 % vanillin conversion in the absence of Hg, demonstrating the inactivation of the Pd-NPs surfaces owing to the formation of a Pd-Hg amalgam by the introduction of Hg(0).

Results and Discussion:

Synthesis of POP and Pd-POP catalysts:

The route for stepwise structural evolution from TRIA-POP to three different Pd-POP materials is schematically presented in the Scheme 1 and the synthetic details were provided in the Experimental Section. Porous Organic Polymer (TRIA-POP) has been synthesized by nonaqueous radical polymerization of 2,4,6-triallyoxy-1,3,5-triazine in the presence of divinylbenzene as cross-linking agent under metal-free and template-free solvothermal conditions using Azobisisobutyronitrile (AIBN) as a radical initiator following the method as previously reported by Zhao *et al.*^[14a] A solvothermal route in a sealed media has been adopted in our present study where triazine monomers started to polymerize with divinyl

10.1002/cctc.201700186

benzene under moderately high temperature (120°C) and high autoclave pressure in the liquid-phase conditions. A highly cross-linked poly-divinylbenzene-co-triallyloxytriazine organic framework was progressively developed in acetone solvent which is likely to be considered to exhibit both as solvent and as well as template roles. White color solid TRIA-POP sample with open disordered porosity were finally obtained with the slow removal of solvent under the autoclave system during the course of gradual formation of framework material.^[14d] Facile treatment of as-synthesized POP with Pd(OAc)₂ in MeOH afforded vellow color Pd(II)-POP composites. Two weak signals appeared at 26.5 and 179.1 ppm in the ¹³C CP MAS NMR spectrum of Pd(II)-POP composite (Figure S1, SI) could be assigned to the carbonyl and methyl carbons of the incorporated Pd(OAc)₂, respectively. Additional reaction of the composite following three different reduction routes in NaBH₄, HCHO and a stream of H₂ gave rise to blackish brown color materials which are designated as Pd-A, Pd-B and Pd-C, respectively. The Pd contents in Pd-A, Pd-B and Pd-C are 0.213, 0.228 and 0.210 mmol/g, respectively, as measured by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis. Insignificant deviation in the experimental C and N content (%) from the corresponding theoretical values were obtained in the Elemental (C, H & N) analyses (Table S1, SI) of the respective Pd-A, Pd-B and Pd-C materials which could be correlated with the very common phenomenon of porous materials that is the inclusion of guest molecules in the POPs. Similar finding regarding the deviation in elemental analysis result has been observed and reported by Wang and co-workers in their triazol functionalized POP decorated Pd-NPs.^[15] The existence of trapped guest molecules and thermal stability was further confirmed by Thermogravimetric (TGA) analysis. An initial weight loss around 2.8%, 3.5% and 5.6% have been observed (Figure S2A, SI) in the TGA curves of Pd-A, Pd-B and Pd-C, respectively, before 150°C which can be assigned to the removal of intercalated and adsorbed water molecules from the POP. All the three respective Pd-POP materials are thermally stable in nitrogen atmosphere up to 400°C temperature. Our respective POP based material also show exceptional chemical stability after keeping the material in strongly acidic solution circumventing the associated structural degradation, as experimentally evidenced by solid state ¹³C MAS NMR studies (Figure S2B, SI).

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Figure 1. a) Wide angle powder X-ray diffraction spectra, b) 13 C CP Solid State MAS NMR spectra, c) N₂ adsorption/desorption isotherms, and d) the corresponding pore-size distributions of Pd-A, Pd-B and Pd-C materials, respectively. Pore Size distributions calculated by NLDFT method.

Porosity and Nanostructure:

Wide angle powder XRD patterns of Pd-A, Pd-B and Pd-C materials (Figure-1a) exhibit three types of characteristic diffractions at 2 Θ values of 40.1°, 46.2°, and 67.2° which could be indexed to the (111), (200), and (220) crystalline reflections, corresponding to the face centered cubic lattice arrangement of Pd (0) NP (JCPDS no. 46-1043).^[16] The additional broad diffraction peak appeared at 2 Θ =20.2° which could be attributed to the pi-stacking of the aromatic building blocks in small domains. The size of the Pd NPs was measured to be approximately 2.76-3.35±0.5 nm with the consideration of most highest intensity diffraction peak of the (111) crystalline lattice plane by using Debye Scherrer equation, which is in good agreement with the results of TEM and HAADF-STEM analysis of the respective Pd-A, Pd-B and Pd-C materials. It is interesting to notice that the Pd (111) and Pd (200) crystalline

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reflections in Pd-B material appeared with the stronger peak intensity than that of the corresponding Pd-A and Pd-C. This observation could be recognized to the deposition of most of the large Pd-NPs on the external surface of POP rather than inside of cavity, resulting a great exposure of Pd-NP in surface.^[17] The weak intensities of (111) and (200) Bragg diffractions for Pd-C material confirm to the well distribution of small size Pd-NPs with the coverage of POP framework, attributing to the minimum exposure of Pd nanocrystal in surface. FT-IR spectra of the Pd-A, Pd-B, and Pd-C materials are displayed in Figure S3, SI. The absorption bands positioned at 1572, 1350, and 807 cm⁻¹ could be recognized for the presence of characteristic triazine framework in all the metal-POP composite materials.^[18] The concomitant appearance of distinguishable peaks at 2927 and 2854 cm⁻¹ are suggestive to the stretching vibrations of the -CH₂ and -CH groups in the aliphatic moiety.^[6c] The molecular connectivity, structural integrity of 1,3,5-triazolyl moiety and different chemical environment of carbon nuclei of Pd-NP fabricated POP materials were assessed by performing Solid state ¹³C CP MAS NMR analysis. ¹³C CP MAS NMR spectra of TRIA (POP) support, Pd-A, Pd-B and Pd-C materials were displayed in Figure-1b. Three broad signals appeared at 112.0, 126.8, and 136.7 ppm are assigned to the characteristic aromatic carbon atoms of the porous organic polymer (overlap of C7-C9) and the signals centered at 28.3 and 39.7 ppm correspond to the different aliphatic carbon atoms (overlap of C3-C6) of the bridging unit. The concurrent emergence of characteristic peak at 144.1 ppm can be attributed to the triazine carbon atom (C1) of the melamine unit, which is consistent with previous analogous reports by Mondal et al. [14a] Rest of these three peaks, the presence of one small peak at 68.3 ppm (Figure-1b) likely refers to the carbon atom (C2) of the -OCH₂ bridging unit. According to FT-IR and solid state ¹³C CP MAS NMR spectral data, we could be able to conclude that the structural integrity of the polymer back bone unit remains undisturbed after Pd modification. The porous properties of Pd-A, Pd-B and Pd-C have been investigated by N₂ adsorption/desorption analysis at 77K (Figure-1c). Nitrogen-sorption isotherms of Pd-A, Pd-B and Pd-C materials, respectively, measured at 77 K exhibited a rapid uptake at high pressure region of $P/P_0 > 0.4$, (Figure 1c) which suggests the presence of inter particle void space within the POP based materials. This sorption profile is described as a type II isotherm, which is the characteristic of porous materials. The appearance of small hysteresis loop in the isotherm could be ascribed to the deformation and swelling of the polymeric network upon the gas adsorption or due to porosity originating from the interparticle void space.^[17, 19] A similar finding regarding this characteristic hysteresis loop in

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the isotherm was previously reported by Bhaumik et al. in nitrogen rich porous organic polymer.^[20] The BET (Brunauer-Emmett-Teller) surface areas of the three materials Pd-A, Pd-B and Pd-C were found to be 542 m²g⁻¹, 491 m²g⁻¹ and 456 m²g⁻¹, respectively. Substantial decrease in the surface areas of Pd-POP materials compared with the parent POP material (The BET surface area of the TRIA material is 620 m²g⁻¹) suggests to both partial pore filling and mass increment after palladium loading. The preservation of N2 adsorption/ desorption isotherms shapes of Pd-A, Pd-B, and Pd-C (Figure 1c) materials signifies no considerable alteration of the pore systems by the occupation of palladium NPs inside the nanocage. The pore volumes of Pd-A, Pd-B and Pd-C materials were evaluated to be 0.46 cm³g⁻¹, 0.39 cm³g⁻¹ and 0.33 cm³g⁻¹, respectively. The pore size distributions of the respective Pd-POP based materials have been calculated from the adsorption branches by employing NLDFT (Non Local Density Functional Theory) method which is presented in the Figure 1d. The corresponding pore-size distributions reveal the narrow pore size distribution with the pores predominately in the microporous range (1.26 nm), which is in good agreement with the shape of N₂ isotherms. A contraction in the pore width in the Pd-POP materials compared with the as-synthesized POP material (Calculated NLDFT pore size for TRIA POP is 2.9 nm) was observed, thus indicating partial occupancy of nanocages with the introduction of Pd nanoparticles in parent POP material. We also note that this observation is in full agreement with the recent work by Shall and co-workers on incorporation of Palladium nanoparticles with the shrinkage of pore sizes within sulfonic acid-functionalized MIL-101(Cr).^[10]



Figure 2. a) XPS survey spectra, b) XPS spectra N 1s region, c) O 1s region and Pd 3d region for d) Pd-A, e) Pd-B and f) Pd-C, respectively.

XPS analysis:

Further insights into the evaluation of oxidation state, metal support interaction and change in the catalyst structure were revealed from XPS measurements. The X-ray photoelectron spectroscopy (XPS) results of the three respective materials Pd-A, Pd-B and Pd-C are provided in the Figure 2. The binding energy peaks in the survey spectra appeared at 284.9, 397.8, 530.8 and around 338.4-339.3 eV could be assigned to the C 1s, N 1s, O 1s and Pd 3d, respectively (Figure 2a). All the binding energies were calibrated via referencing to C 1s binding energy (284.9 eV). The presence of N 1s binding energy peak at 397.8 eV of the as-synthesized POP material corresponds to the single type symmetrical pyridinic N atoms of the 1,3,5-triazine unit (Figure 2b). The XPS spectra of the N-1s core level of the three Pd-POP based materials indeed showed a positive displacement by 0.6 and 1.5 eV, respectively, in comparison with the as-prepared POP, demonstrating strong interaction between the N-rich POP support and Pd-NPs (Figure 2b). It has also been noticed that the interaction between support and Pd-NPs remarkably enhanced with the change of respective synthesis procedure, referring to the strong co-ordination of small Pd-NPs in Pd-C material inside the nanoporous channel. The O 1s spectral regions (Figure 2c) of the respective Pd-A, Pd-B and Pd-C materials reveal a significant contribution in co-ordination with the Pd-NPs of the allyloxy unit from the polymeric framework, as is evident from the O 1s binding energy positive shift compared with the parent POP, which is further supported with previous report in Urea-Based Porous Organic Frameworks.^[21] To have a clear insight in the oxidation state of surface palladium NPs in the respective Pd-POP materials we have carried out XPS spectra in Pd 3d binding energy core (Figures 2d, 2e & 2f). Two sets of spin-orbit doublet could be recognized from Pd $(3d_{5/2,3/2})$ binding energy signals with the intensity ratio at 3:2 considering spin-orbit separation of 5.2 eV. The low-binding-energy doublets of Pd 3d_{5/2} and Pd 3d_{3/2} (Figures 2d, 2e & 2f) appeared at 335.35, 335.56 and 334.92 eV as well as 340.71, 340.75 and 340.23 eV for Pd-A, Pd-B and Pd-C, respectively, could be accepted to the formation of Pd (0) species in the nanohybrids, while the characteristic peaks of Pd $3d_{5/2}$ binding energies at 336.61, 336.64 and 336.50 eV, respectively, pointed at the possibility for the presence of Pd (II) species. In comparison with that in Pd-A and Pd-B, a lower binding energy shift of about 0.44 eV in Pd-C in the Pd 3d XPS spectrum (Figure 2f) was observed which may be assigned to the strong electron-donation effect of nitrogen atoms to small size

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Pd(0) NPs distributed inside the nano cavities of the POP, resulting in more electron-rich Pd(0) species in Pd-C. Very recently, Wang and co-workers have observed similar trend of negative binding energy displacement in Pd 3d spectrum for Pd-POP based materials with stronger interaction between nitrogen atoms and small size palladium NPs present in the interior pores of the POP material.^[22] The ratios of Pd(0) to Pd(II) in Pd-A, Pd-B and Pd-C are 1.96. 1.02 and 0.61, respectively. The occurrence of this Pd (II) species in Pd 3d XPS spectra of the Pd-POP catalysts could be recognized to uniformly distributed single site isolated Pd strongly interacting with the allyloxy triazine moiety through O or N atoms which is in good agreement with the recent results of Bulusheva *et al* for their N-Doped Carbon supported Pd catalyst.^[23] Very recently, Arrigo *et al*. have investigated variation in spectral studies of N atoms after Pd deposition on support which could be attributed to N-Pd covalent bond formation owing to strong interaction between pyridinic N atoms and Pd, with the subsequent outcome of Pd 3d binding energy shift very close to divalent Pd and they have also concluded that the coordination of Pd(II) species to nitrogen of the support makes it difficult in reduction.^[24]

Electron microscopic analyses:

In order to investigate the distribution, shape, location of Pd-NPs on the polymer matrix and their average particle sizes we have conducted Transmission Electron Microscopy (TEM) analysis of the respective Pd-POP materials (Figure 3). TEM images illustrate black color Pd-NPs in Pd-A (Figure 3A-C), Pd-B (Figure 3F, G) and Pd-C (Figure 3K, L) are strongly encapsulated with their mean particle sizes 3.33 ± 0.5 , 8.0 ± 0.33 and 2.71 ± 0.25 nm, respectively on the POP surface. A dual size and homogeneous distribution of Pd-NPs with the average sizes 1.31 ± 0.36 and 2.71 ± 0.25 nm, respectively, has been observed from the TEM images of Pd-C (Figure 3K & L), where relatively small Pd-NPs (1.31 nm) are accommodated in the interior cavities and comparatively large Pd-NPs (2.71 nm) are deposited on the external surface of POP. On the basis of Wang and co-workers previous reports we can assume that selection of H₂ as the reducing agent may promote the particle nucleation within the nanoporous channel under solid-phase conditions by nano-confinement effect of POP, thereby restricting the unnecessary growth of Pd-NPs in Pd-C material.^[22] In contrast, there is an obvious aggregation and worse dispersion of palladium in Pd-B (Figure 3G) leading to the formation of large Pd-NP (8-10 nm with mean particle size) than the Pd-A and Pd-C which could be explained by stabilization of Pd-NPs on the basis of nitrogen



content variation as measured from C, H, N elemental analysis (Table S1, SI) and this phenomena has already been shown and discussed by Zhang *et al.*^[25]

Figure 3. TEM images (A, B & C), (F & G), (K & L) and corresponding HR-TEM images with clear lattice fringe (D), (H & I), (M & N) and SAED patterns with marked facets (E), (J), (O) of Pd-A, Pd-B and Pd-C materials, respectively. Average particle size distributions (P, Q and R) of Pd-A, Pd-B and Pd-C materials, respectively. High magnified TEM image (S) of single Pd nanoparticle of Pd-B. Scale bars (A, 20 nm), (B, 50 nm), (C, 20 nm), (D, 2 nm), (F, 200 nm), (G, 50 nm), (H, 5 nm), (I, 5 nm), (K. 100 nm), (L, 20 nm), (M, 2 nm), (N, 2 nm).

Also Pd-A material exhibits a better homogeneous distribution (Figures 3B & C) but with the larger particle size (3.33 ± 0.5) than the Pd-C, which is probably ascribed to the fact that aqueous solution of NaBH₄ cannot access internal pores efficiently by capillary force due to the hydrophobic nature of nanoporous polymer, causing diffusion of the Pd-NPs and their precursors from interior cavity to the external surface of the polymer, resulting the formation of large particle size.



Figure 4. HAADF-STEM images with the corresponding elemental mapping of C, N, O and Pd for A) Pd-**A**, B) Pd-**B** and C) Pd-**C** materials, respectively.

The morphology and crystalline feature of the anchored Pd-NPs was further established at a closer view from the High Resolution (HR) TEM images (Figures 3 D, H, I, M & N) of the respective Pd-POP materials which demonstrate that the distinguished lattice fringes with the d spacing about 2.14Å for Pd NPs, clearly assigning to the (111) lattice spacing of face centered cubic (*fcc*) arrangement of the Pd(0) nanopartciles. Characteristic bright rings associated with distinct spots are obviously observed in the Selected Area Electron

Diffraction (SAED) Patterns (Figure 3E, J & O), which could be readily indexed to the corresponding (311), (400), (222), (200), (331), (220), (111) crystalline reflections planes of *fcc* Pd.^[26] The average Pd NPs size distributions of the Pd-A, Pd-B and Pd-C materials are displayed in the inset of Figure 3P, 3Q and 3R, respectively. From the above TEM images analysis we can definitely conclude that the synthesis method by varying the reducing agents from NaBH₄, HCHO to H₂ exhibits a considerable effect on the size and dispersion of NPs. High-angle annular dark-field scanning TEM (HAADF-STEM) images of the respective Pd-A, Pd-B and Pd-C materials (Figure 4) reveal that the as-synthesized POP was decorated with uniformly distributed palladium NPs (bright spots). The existence of evenly distributed Pd NPs in the nitrogen rich carbon matrix can be further confirmed from their corresponding EDX (Energy Dispersive X-ray) elemental mapping analysis (Figure 4). The particle size distributions measured from the respective HAADF-STEM images clearly indicate to the existence of similar average particle size with a very negligible difference as determined from the conventional TEM images.

Catalytic Hydrodeoxygenation (HDO) of Vanillin with Pd-POP based catalysts:

We have investigated the catalytic performance of our newly designed Porous Organic Polymer decorated Pd nano catalysts in biofuel upgrading considering liquid phase hydrodeoxygenation of Vanillin into 2-methoxy-4-methylphenol, a typically model component of pyrolysis oil derived from the lignin fraction. The catalytic transformation of the C=O to $-CH_3$ group is involved with the three different path ways which includes i) hydrogenation/dehydration, (ii) hydrogenation/hydrogenolysis, and (iii) direct hydrogenolysis of the C=O bond, respectively. Hydrogenation/dehydration pathway is not feasible due to absence of α -hydrogen in the reduced product vanillin alcohol. So the progress of the transformation from vanillin to 2-methoxy-4-methylphenol must be involved either by hydrogenation/hydrogenolysis or direct hydrogenolysis. Our initial experiment began by conducting hydrodeoxygenation (HDO) reaction of Vanillin (100 mg, 0.657 mmol) with isopropanol (30 mL) over Pd-A nano catalyst in a stainless steel reactor inbuilt with a pressure gauge setup under 10 bar hydrogen pressure at 140°C temperature. The corresponding Pd-B and Pd-C catalysts were also tested under the identical reaction conditions for comparison study. The contents of products and reactants were determined using a GC-FID based on authentic samples. Among the diverse Pd-POP based catalysts investigated, the Pd-C exhibits superior catalytic performance in HDO reaction of vanillin providing conversion (96%) and selectivity (98%) to the desired product 2-methoxy-4-

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methylphenol, affording a magnitude TOF of 8.51 h^{-1} (Figure 5A). On the other hand, we have achieved a 91% and 84% conversion of vanillin with 98% and 86% selectivity of 2methoxy-4-methylphenol after 18 h reaction time for the corresponding Pd-A and Pd-B catalysts, exhibiting TOF values of 7.18 h⁻¹ and 6.72 h⁻¹, respectively. When we have evaluated the catalytic activity of bare Pd-NPs in HDO reaction of vanillin under optimized reaction conditions, the vanillin conversion was drastically decreased to 16% with a targeted product selectivity of 85%, displaying a TOF value of 1.39 h⁻¹ (Figure 5A). The superior catalytic performance of Pd-C can be attributed not only due to its higher nitrogen content which facilitates improved homogeneous dispersion of smaller mean size of Pd-NPs, but also due to the existence of electron-rich Pd formed by the strong electronic interaction between Pd and N atoms from 1,3,5-triazine unit, favouring preferential hydrogenation over the electron-enriched metallic Pd, supported with the previous reports by Tsang et al.^[27] The existing electron transfer from nitrogen functional group of the support to the Pd was further confirmed by the higher positive and negative displacement in XPS binding energies of N and Pd core regions of Pd-C compared with the other catalysts. Similarly Arrigo and coworkers have found that the N-Pd interaction in Pd nanoparticles immobilized on N-doped carbon nanotubes was responsible for the enhanced catalytic activity in acetylene hvdrogenation.^[24] Small size Pd-NPs (1.31 nm) in the Pd-C catalyst may play a decisive role for the improved catalytic performance compared with the other catalysts which possess large size Pd-NPs (3.33-10 nm) on the external surface of the POP owing to their high surface-tovolume ratio with huge number of available active sites per unit area for reaction substrates. Shall and co-workers have investigated that large Pd-NPs (5.5 nm in size) distributed on the outer surface of Pd/NH₂-UiO-66 provided a lower catalytic activity and selectivity of desired product in HDO of vanillin compared with the embedded Pd-NPs inside the cavity of NH₂-UiO-66 having mean size in the range of 1.5-2.5 nm.^[9] Similar conclusion has been drawn regarding the higher catalytic activity of Pd@MIL-101 in HDO of vanillin where smaller Pd-NPs with an average size of 1.8 ± 0.2 nm are accommodated inside the mesoporous cavities of MIL-101 than the large particles present on the external surface.^[12] Following these observations, we can emphasize that small Pd particle size become the determining factor for such higher activity which resembles well for the poor activity in Pd-B. In order to validate the feasibility of involved catalytic pathway for the hydrodeoxygenation of vanillin over the newly designed Pd-POP catalysts, we have further examined the distribution of substrate and product selectivity as a function of reaction time, influence of the reaction temperature and

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effect of hydrogen pressure. Evolution in the reactant and product distributions with the progress of the reaction as a function of reaction time over the Pd-**A**, Pd-**B** and Pd-**C** catalysts are provided in the Figures 5B, 5C and 5D, respectively.



Figure 5. A) Comparison in catalytic activity with respect to TOF (turn over frequency) for vanillin hydrodeoxygenation reaction with Pd based catalysts; Reaction conditions: vanillin (100 mg, 0.657 mmol), Pd catalyst (20 mg), isopropanol (30 mL), 10 bar H₂ pressure, 140°C, 18 h; Evolution of reactant and product distributions as a function of time over B) Pd-A, C) Pd-B and D) Pd-C catalysts, respectively; Reaction conditions: vanillin (100 mg, 0.657 mmol), Pd catalyst (20 mg), isopropanol (30 mL), 10 bar H₂ pressure, 140°C; E) Influence of reaction temperature with diffrent Pd-POP catalysts in vanillin HDO reaction; Reaction conditions: vanillin (100 mg, 0.657 mmol), Pd catalyst (20 mg), isopropanol (20 mg), isopropanol (30 mL), 10 bar H₂ pressure, 18 h; F) Effect of H₂ pressure on conversion and product selectivity; Reaction conditions: vanillin (100 mg, 0.657 mmol), Pd catalyst (20 mg), isopropanol (30 mL), 140°C, 18 h.

The reaction was accompanied with a progressive increase in vanillin alcohol selectivity (~87-93%) and conversion of vanillin (~10-32%) at initial 3 h, which demonstrates that vanillin, is mainly hydrogenated to vanillin alcohol in the first step. However, in the first 3 h we have noticed appearance of little amount of 2-methoxy-4-methylphenol (~10%), illustrating that vanillin alcohol underwent hydrogenolysis reaction to deliver the desired product. Surprisingly, no peak for 2-methoxy-4-methylphenol at initial 3 h for Pd-**B** catalyst has been observed from the Time-on-stream profile (Figure 5C), suggesting the poorer catalytic activity in hydrogenolysis reaction. The catalytic conversion for this

hydrodeoxygenation reaction could be observed at after 3 h with the very les selectivity of 2methoxy-4-methylphenol but selectivity vanillin alcohol was found to be very high. But after 18 h, all the produced *in situ* vanillin alcohol had been completely transformed into 2methoxy-4-methylphenol *via* hydrogenolysis. These results consistently prove that transformation of vanillin to 2-methoxy-4-methylphenol proceeded by hydrogenation to vanillin alcohol followed by hydrogenolysis.^[28]

The decisive role of reaction temperature in hydrodeoxygenation of vanillin over our newly developed Pd-POP catalysts has been thoroughly investigated by conducting the catalytic reaction at different reaction temperatures ($80^{\circ}C$ - $160^{\circ}C$) under 10 bar H₂ pressure (Figure 5E). An enhancement in catalytic performance for Pd-A catalyst with a high vanillin conversion (~95%) and 2-methoxy-4-methylphenol selectivity of >90% has been achieved, upon raising the temperature from 100°C to 140°C. The examination results of the other two respective Pd-B (from 44% to 84%) and Pd-C (from 52% to 96%) catalysts unambiguously demonstrate the similar accelerating trends in catalytic activity with higher reaction temperature, suggesting much faster reaction kinetics, which can be further enhanced to 100% at 160°C. However, a gradual drop in 2-methoxy-4-methylphenol selectivity (from 91% to 80%) on Pd-A, (from 90% to 83%) on Pd-B and (from 96% to 78%) on Pd-C catalysts, respectively, at 160°C has been observed, which could be attributed to the appearance of Guaiacol, p-cresol and Cyclohexanol by some undesired side reactions including decarbonylation, deeper hydrogenation and hydrogenolysis thereby causing some catalyst deactivation. Previous reports also indicated that elevated temperature offered an acceleration in polycondensation, which was thought to be accountable for the loss in mass balance.^[29] We have performed the catalytic activity of newly developed Pd-POP catalysts for HDO of vanillin with various solvents including isopropanol, water, methanol and isopropanol and water mixture (Table S2, SI). Among these solvents tested isopropanol-water mixture proved to be the best one to provide better conversion under mild conditions (0.7 MPa H₂ and 120 °C) but selectivity of the targeted product is less compared with the isopropanol owing to the high solubility of vanillin alcohol in water. In contrast, we have noticed very poor conversion of vanillin but with very high selectivity of 2-methoxy-4methylphenol in water. Most of the previous literature reports predict that the HDO of vanillin was conducted very efficiently either in water or in water/oil emulsion medium. But in our case the reverse trend is noticed. This new trend could be explained on the basis of type of nitrogen atoms present inside the supported catalytic systems. It has been proposed by

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Jiang and co-workers that polarization effect between graphitic-N and adjacent carbon atoms significantly alter the charge distribution over N-atoms thereby favouring interaction with nucleophilic H₂O molecules and as a result the superior catalytic performance for the carbon nitride based catalyst in vanillin HDO reaction in aqueous medium is observed.^[11] This charge distribution of the N-doped graphitic material exhibits a crucial role in the enhancement of catalytic activity. The absence of graphitic-N atoms rather than the presence of pyridinic-N atoms in our as-synthesized Pd-POP based catalyst has been experimentally evidenced by the appearance of XPS binding energy at around 398.4-399.3 eV in the N-1S spectra (Figure 2b). Kim and co-workers proposed that lone-pair electrons over the pyridinic-N atoms in the catalyst does not take part in favourable interaction with the water molecules, resulting in poor contact with the substrates and suppression of the catalytic activity.^[30]

Different hydrogen concentration (3-15 bar) were subsequently screened on vanillin hydrodeoxygenation at the optimized temperature of 140°C (Figure 5F). It is noticed from the Figure 5F that, in the presence of hydrogen environment i.e., without any pressure showed poor activity indicating hydrogen pressure is essential for the improvement of catalytic activity. An increase in H_2 pressure (from 5-10 bar) led to an enhancement in vanillin conversion and selectivity of 2-methoxy-4-methylphenol. However, with further increase of hydrogen pressure above 10 bar remarkably decreased the 2-methoxy-4-methylphenol selectivity, with the subsequent enhancement in undesired side products (e.g. Guaiacol and anisole) selectivity including over-hydrogenation and decarbonylation pathway owing to the availability of high concentration of hydrogen. Encouraged with this promising result and considering that Pd-based materials can serve as an effective catalysts in hydrodeoxygenation of vanillin, we have synthesized a series of supported Pd catalysts following the solid phase H₂ reduction method and investigated their catalytic activity under our standard reaction conditions. The comparison study with various Pd based catalysts including Pd-C, Pd-SiO₂, Pd-CeO₂, Pd-TiO₂, are summarized in Figure 6A. The textural proprieties of the conventional catalysts are provided in the Figure S4, SI. When Pd-C and Pd-SiO₂ have been utilized, we have achieved 84.7% and 82.1% conversion with 76.7% and 47.3% selectivity of desired product, respectively. The observed poor selectivity of targeted product below 30% for the catalysts of Pd-CeO₂ and Pd-TiO₂ could be delineated as the some extent of vanillin alcohol are not fully converted to produce 2-methoxy-4-methylphenol. The observed relatively low selectivity towards the targeted product (Figure 6A), probably due to their poor wettability, low mass transfer, less surface area, poor dispersion of nanoparticles, less metal-support

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interaction and large Pd NPs. Some aggregation of Pd-NPs was noticed from the TEM images of the conventional catalysts (Figure S4, SI) which could be pointing out towards the poor catalytic activity. Although the reference catalysts provided satisfactory product conversions but didn't show long-term durability in succession of several catalytic runs. Leaching of Pd-NP from the reference catalysts has also been found out owing to the absence of strongly anchoring sites causing to the diminishment in catalyst recyclability. Delightedly, oxides supported Pd NPs were found to be reasonably effective for this catalytic bio-fuel upgrading reaction, furnishing 2-methoxy-4-methylphenol in lower conversions than Pd-POP (Figure 6A), inferring that the N dopant for the catalysts played a pivotal role for this catalytic reaction. Compared with the highly conventional solid catalysts, doping with N atoms enhanced the hydrophilic nature of Pd-POP, homogenous dispersion and stabilization of Pd-NPs, which could improve the catalyst dispersion along with the maximum exposure of catalytic active sites to the substrates (e.g., vanillin), thereby increasing the catalytic performance significantly. Our explanation is in good agreement with the improved catalytic activity of Pd@CN_{0.132} compared with the conventional catalysts in vanillin hydrodeoxygenation reaction as reported by Wang *et.al.*^[7]

The superior catalytic performance of Pd-POP catalyst compared with the other conventional catalysts can be attributed to the homogeneously distributed electron-rich metallic Pd sites offering excellent hydrogenation activity and high surface area and hierarchical pores facilitates hydrogenolysis of the intermediate to the desired product with fast and easy diffusion. The high catalytic activity can also be explained by easy adsorption of organic substrates onto the nanoporous matrix by hydrophobic interactions and from π - π interactions between aromatic aldehyde and aromatic POPs framework. We have previously reported this special advantage of the POP based catalysts in nitrobenzene and alkene hydrogenation reactions with Ru-POP and Pd-POP based catalysts.^[14a,14g] We have also examined vanillin hydrodeoxygenation reaction of Pd/POP (Figure 6A), has been developed by employing a physical mixture of triazine based polymer and Pd NPs, but surprisingly only 36.7% conversion with 26% and 70% selectivity of 2-methoxy-4-methylphenol and vanillin alcohol, respectively, has been attained after 20 h. The greater catalytic efficiency of the Pd@POP material than Pd/POP can be ascribed to the synergetic effects of nano-confinement and electron-donation offered by the POP framework, making the Pd surface more electron rich and active, thereby facilitating for the effective hydrogenation reaction. This finding supports the previous assumption of the Xu research group associated with the efficient

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Entry	Catalyst	Con (%)	Selectiv	Selectivity (%)	
			Alcohol	Cresol	
1	Pd/MSMF	>99.5	45.8	54.2	8
2	Pd/CN _{0.132}	65	31	69	7
3	Pd/SWNT-SiO ₂	85	53	47	31
4	Pd/SO ₃ H-MIL-101	96.1	9.1	90.9	10
5	Pd@NH ₂ -UiO-66	100	0	100	9
6	Pd/NPC-ZIF-8	100	0	100	11
7	Pd-POP	96.5	1.8	98.2	Our Work

 Table 1: Comparison in catalytic performance for Hydrodeoxygenation of vanillin over different catalysts

vanillin HDO reaction where higher quantity of vanillin alcohol has been observed for the Pd-NPs with better accessibility but no nano-confinement effect in Pd/MIL-101 owing to a weak interaction between the reactant and active centres.^[12] Furthermore, we have carried out the comparison study in the catalytic performance, desired product selectivity over the newly developed Pd-POP catalyst and as well as catalyst durability with those reported in the literature (Table 1). The survey reports indicated that a 99.5% conversion of vanillin with 54.2% 2-methoxy-4-methylphenol selectivity could be achieved over 4.5 wt% Pd/MSMF catalyst (entry 1 in Table 1) by Xiao *et al.*^[8] Additionally, superior catalytic performance for our developed catalyst compared with the N-doped carbon-supported Pd catalyst and palladium nanoparticles deposited onto the SWNT-inorganic oxide hybrid catalyst (Pd/SWNT-SiO₂) has been observed (entries 2 and 3, Table 1).^[31] On the other hand, Shall and co-workers have investigated hydrodeoxygenation of vanillin over Pd/SO₃H-MIL-101

catalyst and a 96.1% conversion of vanillin with lower selectivity (entry 4, Table 1) for 2methoxy-4-methylphenol has been achieved.^[10] In contrast, Pd@NH₂-UiO-66 catalyst as prepared by Shall and co-workers exhibits a remarkably high

Table 2: Use of different hydrogen source for hydrodeoxygenation of vanillin with Pd-POP

 Nanocatalyst

Entry	Catalyst	H ₂ Source	H ₂ Source Con (%) Sel		ectivity (%)	
				Alcohol	Cresol	
1	Pd-A	HCOOH ^a	40.3	79.4	20.6	
2	Pd- B	HCOOH ^a	32.8	83.7	16.3	
3	Pd-C	HCOOH ^a	49.6	76.3	23.7	
4	Pd-A	ⁱ PrOH ^b	59.7	70.8	29.2	
5	Pd -B	ⁱ PrOH ^b	45.6	65.7	34.3	
6	Pd-C	ⁱ PrOH ^b	63.2	79.6	20.4	

Reaction conditions: ^{*a*}vanillin (100 mg, 0.657 mmol), Pd catalyst (0.014 wt% of Pd), HCOOH (3.28 mmol, 0.3 mL), EtOH, 120°C, 15 h, under sealed-tube conditions; ^{*b*}vanillin (100 mg, 0.657 mmol), Pd catalyst (0.014 wt% of Pd), ^{*i*}PrOH(30 mL), 150°C, 15 h, under high pressure autoclave condition.

catalytic activity and selectivity for 2-methoxy-4-methylphenol (entry 5, Table 1) but the durability of the catalyst in terms of recyclability does not show any impressive result.^[9] The same phenomenon has been observed for the Pd/NPC-ZIF-8 catalyst (catalyst could be recycled for only three successive runs) as reported by Jiang *et al.* (entry 6, Table 1).^[11] The long term durability of our new catalyst in the 10th catalytic run for succession compared with the previously reported catalysts could be explained on the basis of strong catalyst support interaction which is strongly dependent on the configurations of the N-dopants inside the

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highly crosslinked rigid polymer materials. It has been well documented that pyridinic-N atoms bind more strongly with the transition metal than the other type of nitrogen atoms owing to the larger overlap between nonbonding state of lone pair electrons and the d-orbital of the transition metal.^[32] These newly designed Pd-POP catalysts hold promising potential for biofuel upgrade processes, and additional work will be conducted toward the applications to natural lignins and other model compounds. We have further examined the catalytic activity of our newly designed Pd-POP catalysts in hydrodeoxygenation of vanillin (Table 2) by employing various hydrogen sources including alcohol, formic acid, which can donate hydrogen to reduce the substrate in a process called catalytic transfer hydrogenation (CTH). HCOOH and ⁱPrOH both were considered as the poor hydrogen sources in HDO of vanillin providing around 40-50% and 60-65% conversion, respectively, with higher selectivity for vanillin alcohol. But the past decade has witnessed that the hydrodeoxygenation of vanillin to 2-methoxy-4-methylphenol, a potential future biofuel could be executed in the presence of Formic acid is a remarkable bio-derived source of hydrogen employing AgPd@g-C₃N₄ and (Pd/TiO₂@N-C) catalysts under visible light and UV light mediated reaction conditions.^[33]

Catalyst reusability:

The outstanding catalytic performance of Pd-**A**, Pd-**B**, and Pd-**C** encouraged us to investigate their stability and recyclability, which are also important aspects in heterogeneous catalytic systems. In order to evaluate the recyclability of the newly designed Pd-POP systems we have conducted the HDO reaction of vanillin under the applied batch conditions and the results are provided in the Figure 6B. The solid catalyst was recovered after the reaction by centrifugation technique followed by washing with methanol 2-3 times, dried at 80°C in oven overnight, and used for the next cycle reaction in succession. The detail about the recyclability test has been provided in the Experimental Section. Under these conditions, our Pd-C catalyst could be recycled in successive ten runs (Figure 6B) sustaining 2-methoxy-4-methylphenol selectivity and yield. Only a little drop in vanillin conversion from 96.5 to 91.9% was observed upon the seventh reuse (Figure 6B). In contrast, Pd-**B** and Pd-**A** catalysts could also be reused for fifth and seventh consecutive catalytic runs, affording a significant decrease in conversion from 84.3 to 61.2% and 91.2 to 75.3%, in the fifth and ninth runs, respectively. On the other hand from the above investigation we can conclude that Pd-C is highly stable catalyst compared with the others providing a near-quantitative



Figure 6. A) Comparison study in catalytic performances with various supported Pd nanohybrid catalysts, Reaction conditions: vanillin (100 mg, 0.657 mmol), Pd catalyst (20 mg), isopropanol (30 mL), 10 bar H₂ pressure, 140°C, 18 h; B) Recycle potential diagram for catalytic hydordeoxygenation of vanillin with Pd-A, Pd-B and Pd-C catalyts, respectively; Reaction conditions: vanillin (500 mg, 3.375 mmol), Pd catalyst (100 mg), isopropanol (150 mL), 10 bar H₂ pressure, 140°C, 18 h; C) Evolution of reactant and product distributions in recyclability test for Pd-C catalyst; D) Hot-filtration experiments where Pd-C catalyst was removed after 6 h and 18 h followed by addition of vanillin (100 mg, 0.657 mmol), Pd catalyst (20 mg), isopropanol (30 mL), 10 bar H₂ pressure, 140°C, 18 h.

2-methoxy-4-methylphenol yield up to the tenth recycling run. Figure 6C suggested that selectivity of the desired product and intermediate is nicely preserved in each catalytic run. A slight drop in the vanillin conversion and desired product selectivity for Pd-C in the recycling test at tenth cycle could be attributed to the accumulation of carbonaceous deposits on the catalyst surface or slight trapping of residual reactants or products inside the pores thus blocking the accessibility of active sites.

Reused Catalyst Characterization:

We have performed TEM analysis of the respective recycled catalysts after consecutive catalytic reactions in order to check the location, distribution and stability of Pd-NPs of these catalytic systems (Figure 7). It is quite evident from the Figures 7A & B, the mean sizes of palladium particle uniformly dispersed on the external surface in Pd-A catalyst are slightly increased from 3.33 to 3.54 nm after 7th catalytic run. In contrast, a severe agglomeration of Pd-NPs for Pd-B catalyst has been observed after 5th catalytic run thereby increasing the average particle sizes from 8.65 to 12.73 nm (Figures 7C & D). The increase in mean particle size and severe aggregation of palladium nanoparticles signify to the drastic drop in conversion (%) during the course of recyclability test for Pd-B catalyst. However, the average palladium NPs size in Pd-C increases to (3.22±0.43) nm compared with the fresh one after the tenth reaction cycle (Figures 7E & F), which may be attributed to the diffusion out of the small palladium NPs from the interior cavity and deposition on the external surface during the consecutive reaction resulting an increase in mean particle size. This observation nicely resembles with the reported NPs encapsulated in the interior pores of POPs by Wang et al.^[34] The impressive Pd-C catalyst stability during the consecutive reaction cycles could be emphasized on the basis of the nano-confinement effect of the host framework and the strong interaction of nitrogen rich 1,3,5-triazine linkage to encapsulated Pd-NPs thereby making them leaching resistant. ¹³C CP solid state MAS NMR characterization study of the reused catalysts (Figure S5, SI) revealed the mechanical and chemical stability, evading the associated structural degradation of the catalyst.



Figure 7: TEM images of reused Pd-A (A & B) after 7th catalytic run, Pd-B (C & D) after 5th catalytic run and Pd-C (E & F) after 10th catalytic run, respectively.

In order to access the robustness and heterogeneous nature of the designed Pd-POP catalysts we have conducted Hot filtration and Hg (0) poisoning test under optimized reaction conditions. Typically, in the hot-filtration test, we have stopped the recation releasing the hydrogen pressure from the stainless steel reactor after 6 h, followed by cooling down at room temperature. The black solid was separated from the reaction mixture by centrifugation. 54.6% vanillin conversion after 6 h has been reached (Figure 6D). Then we have continoued

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the reaction with the filtrate but no further improvement in vanillin conversion to either vanillin alcohol or 2-methoxy-4-methylphenol beyond 55% was noticed. Our investigation obviously demonstrates about the limited leaching of Pd in the reaction mixture during the course of reaction, with the appearence of very trace amount Pd in the reaction mixture making the filtrate solution light brown in color. But it was found that the Pd content in the filtrate was below the detection limit as measured by AAS (atomic absorption spectroscopy) analysis instrument. In order to evaluate the active nature of the homogeneously leached Pd species we have again added excess amount of vanillin into the filtrate and further continoued the reaction for another 20 h under 10 bar H₂ pressure at 140°C. But only ~5-6% vanillin converion to vanillin alcohol was observed after 20 h which validated that an insignificant contribution of leached Pd species in the HDO of vanillin but didn't truly catalyze this reaction up to full conversion level. Inductive Coupled Plasma-optical emission spectrometry (ICP-OES) analysis result suggests Pd content in Pd-A, Pd-B and Pd-C catalysts after the 7th, 5th and 10th catalytic runs are 0.192 mmol/g, 0.175 mmol/g and 0.190 mmol/g, respectively. We have also conducted a standard Hg-poisoning test for the successful inhibition of the catalytic reaction, indicative of Pd-POP catalysts are indeed heterogeneous in nature. The detail procedure is provided in the Experimental Section. When one drop of Hg(0) was introduced to the reaction mixture in the autoclave system, it was found that the achieved vanillin conversion was poor than that was carried out in the absence of mercury under the identical reaction conditions, signifying the inactivation of the Pd-NPs surfaces due to the formation of Pd-Hg amalgam by the introduction of Hg(0).

Conclusion: In summary, we have successfully achieved immobilization of ultrafine Pd nanoparticles having diameter (2.7-8.2 \pm 0.5 nm) within the cavities and as well as external surface of 1,3,5-triazine functionalized Porous Organic Polymer by following three different NaBH₄, HCHO and H₂ reduction routes, respectively, which exhibited an impressive catalytic activity and selectivity for hydrodeoxygenation of vanillin, a common component in ligninderived bio-oil, displaying a TOF value of about 8.51 h⁻¹. It was experimentally evidenced from the TEM images that the Pd-NPs having dual size (1.31 \pm 0.36 and 2.71 \pm 0.25 nm) distribution located in the interior cavity and as well as external surface significantly contributed to the high catalytic activities. The impressive catalytic activity was principally attributed to the uniformly-distributed electron-rich metallic Pd sites generated by the electron transfer from the N-rich POP to Pd sites, favouring superior hydrogenation activity, highly rigid cross linked amine functionalized POP framework makes palladium nanoparticles leaching resistant and high surface area and hierarchical pores facilitates hydrogenolysis of the intermediate to the desired product with easy diffusion. Moreover, developed Pd-POP based catalyst show exceptional stability with no leaching of Pd, sustaining 2-methoxy-4-methylphenol productivity and selectivity on multiple re-use for 10th catalytic runs in succession. The present result can encourage further future research for designing of some promising POP encaged Pd catalyst in advanced catalytic applications in biofuel upgrading process and fine chemicals production.

ASSOCIATED CONTENT

Supporting Information The Supporting Information is available free of charge on the ACS Publications website ¹³C CP MAS NMR, C, H, N analysis data, TGA, FT-IR, HR-TEM images of Pd-C, Pd-SiO₂, Pd-CeO₂ and Pd-TiO₂ catalysts, Screening of solvent in catalytic reaction, ¹³C MAS NMR of reused catalyst.

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Notes

The authors declare no competing financial interest.

Acknowledgements

RS and JM thank to Department of Science and Technology, India for DST-INSPIRE Faculty Research project grant (GAP-0522) in CSIR-IICT, Hyderabad. KD wishes to thankfully acknowledge Department of Science and Technology (DST), New Delhi for providing her DST-INSPIRE-JRF fellowship. SCS thanks CSIR, New Delhi for his respective junior research fellowship.

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Graphical Abstract

Palladium Nanoparticles Encaged in Nitrogen Rich Porous Organic Polymer: Constructing Robust Promising Nanoarchitecture in Catalytic Biofuel Upgrade

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Palladium nanoparticles encapsulated within the highly cross-linked Porous Organic Polymer exhibit excellent catalytic activity with superior stability in promoting Biomass refining (hydrodeoxygenation of vanillin, a typical compound of lignin-derived bio-oil).