Supporting Information

Synthesis and Applications of Micro-Pine Structured Nano-Catalyst

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Contents:

General Experimental:

Pine-structured nano-ferrites were synthesized using a Milestone microwave (MW)-oven. The phase of the as-synthesized ferrite nanoparticles was determined by X-ray diffraction in a MMS X-ray diffractometer with a Cu Kα source in the 2θ range 10 to 75. The data were collected with a step of 1 deg/min. A few drops of a methanol dispersion of the as-synthesized nanoparticles were added to a quartz plate and dried at room temperature and used to record X-ray pattern. TEM micrographs were recorded on a JEOL JSM-1200 II microscope at an operating voltage of 120 kV. A drop of the methanol dispersion of the as-synthesized nanoparticles was loaded on a carbon-coated copper grid and then allowed to dry at room temperature before recording the micrographs. FTIR spectra were recorded from 500 to 3000 cm^{-1} by drop-casting a methanol dispersion solution onto polystyrene standard transparent films to confirm the presence of the surface-functionalized moieties on the surface of the nanoparticles. Elemental analyses of the as-synthesized samples were performed on a Perkin Elmer Optima 3300 DV inductively coupled atomic emission spectroscope (ICP-AES). 5 mg of each sample was dissolved in 2.5 mL of aqua-regia and the volume was adjusted to 50 mL. This diluted sample was then used for the elemental analysis.

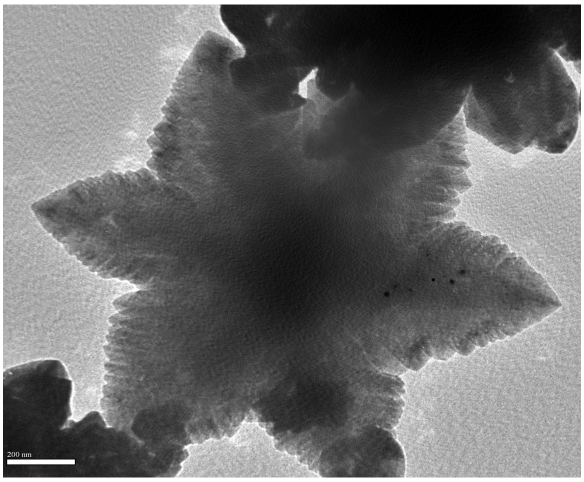
Thin layer chromatography (TLC) (silica gel; 20 % ethyl acetate: hexane) and gas chromatography (GC) were used to monitor the reactions. The product yields were determined by GC-MS. The crude products were identified by GC-MS qualitative analysis using a GC system with a Mass selective detector. The identities were further confirmed for representative compounds by ^1H and ^{13}C NMR spectra that were recorded in deuterated chloroform-*d* ($CDCl_3$) with tetramethylsilane (TMS) as internal reference using a 300 MHz NMR spectrometer. CEM Discover focused MW synthesis system was used to carry out all the organic reactions.

Synthesis of Pine-Structured Nano-Ferrites:

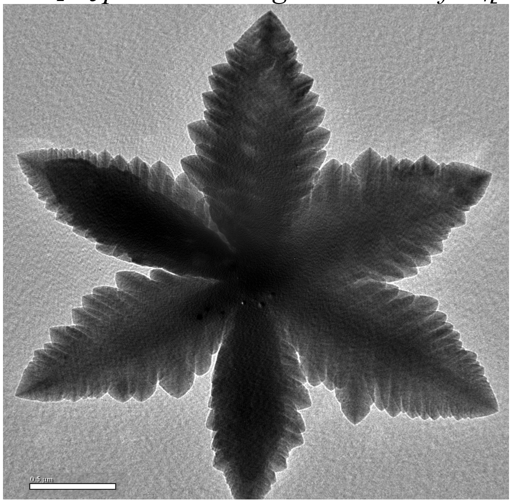
$K_4[Fe(CN)_6]$ was dissolved in distilled water at the desired concentrations (0.01. 0.02, 0.03 moles) and taken in a 50 mL crimp-sealed thick-walled teflon MW-reactor equipped with a pressure sensor and a magnetic stirrer. The reactor was then placed inside Biotage microwave synthesis system, operated at 150 $\pm$ 5 ^oC (temperature monitored by a fiber optics), power 200 to 600 Watt and maximum pressure 20 psi, for 3 h. After completion of the reaction, the product was isolated by centrifugation and washed three times with water and methanol; then dried under vacuum at 50 ^0C for 1 h. (40 % yield).

The effects of substrate concentration and reaction temperature on the morphology of the nanoparticles were also studied. It was observed that with an increase in the concentration, the sharpness of branched dendrite particles decreased and materials with slightly branched particles were formed. Reaction temperature plays a crucial role in this synthesis. At 150 ^{0}C, good product yields were obtained in 3 h; below this temperature, the formation of nanoparticles needed extended reaction time.

TEM image of the synthesized micro-pine α-Fe_2O_3 particles:



TEM of α-Fe_2O_3 particles using 0.01 mole of $K_4[Fe(CN)_6]$



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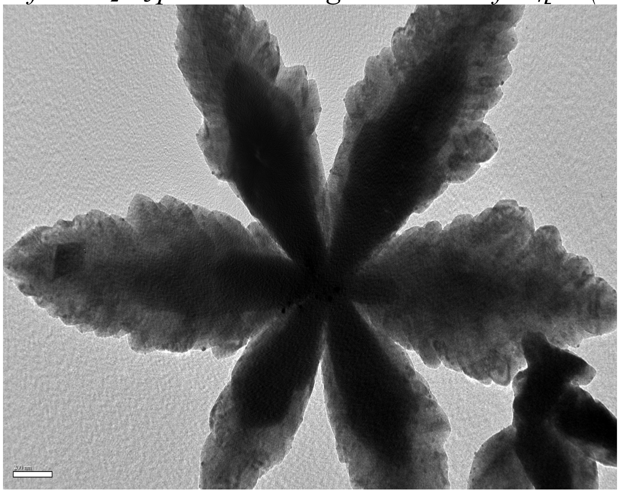


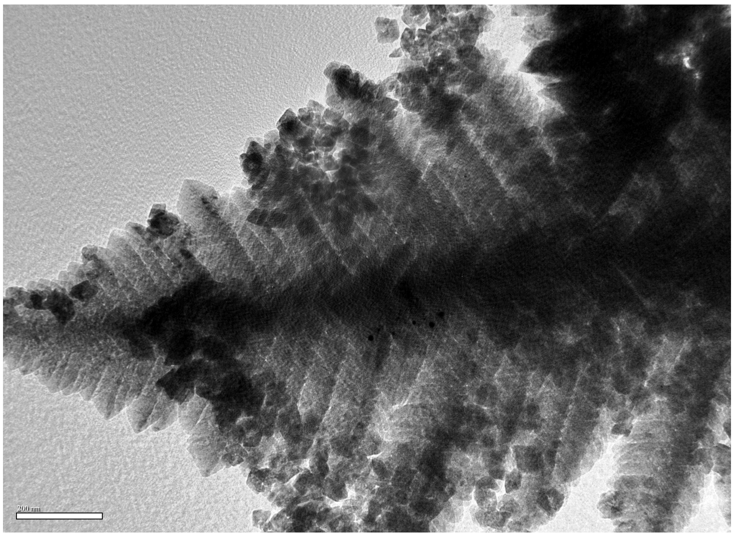
TEM of α-Fe_2O_3 particles using 0.03 mole of $K_4[Fe(CN)_6]$

Surface Modification of Nano-Pine Ferrites:

Pine-structured α-Fe_2O_3 (2 gm) was placed in 25 mL water and sonicated for 30 min. Dopamine hydrochloride (2 gm) dissolved in 5 mL of water was added to this mixture and again sonicated for 2 h. The amine-functionalized nanomaterial was then precipitated using acetone, isolated by centrifugation (90 % yield), and dried under vacuum at 60 ^{0}C for 2 h.

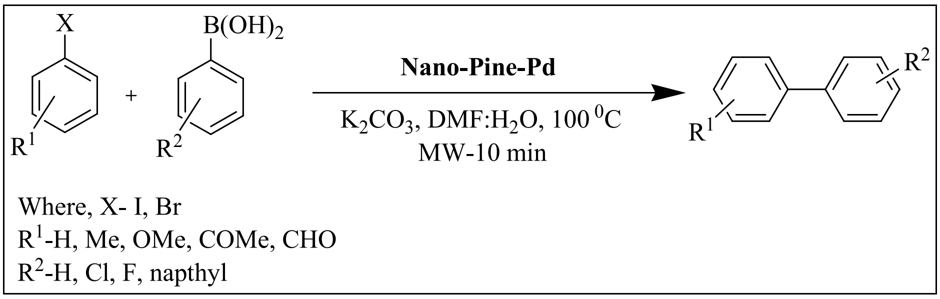
Synthesis of Nano-Pine-Pd Catalyst:

Amine-functionalized α-Fe_2O_3 nanoparticles (1 gm) were dispersed in water and $NaPdCl_4$ solution in water was added to the mixture to get 10 wt % of Pd. Hydrazine monohydrate solution in water was added drop-wise to bring the pH of this mixture to 9. The reaction mixture was then stirred for 24 h at room temperature. The product was allowed to settle, washed several times with water and acetone, and dried under vacuum at 60 ^{0}C for 2 h (80 % yield). The weight percentage of Pd in the catalyst was found to be 7.26 % by ICP-AES analysis. This postsynthetic surface modification yields the palladium decorated system as idealized in Scheme 1 and as confirmed by below TEM image.



TEM of Pd-coated amine-functionalized α-Fe_2O_3 nanoparticles

Suzuki Reaction:



Where, X- I, Br
R^1-H, Me, OMe, COMe, CHO
R^2-H, Cl, F, napthyl

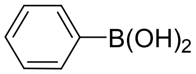
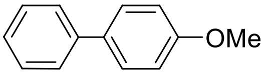
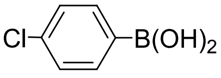
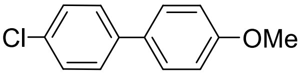
Scheme 1. Suzuki reaction using Nano-pine- Pd catalyst.

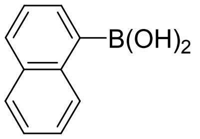
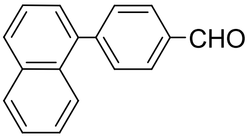
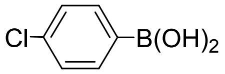
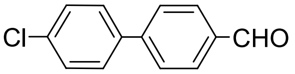
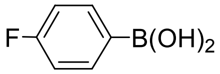
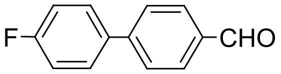
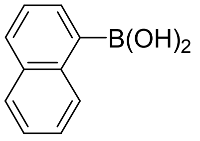
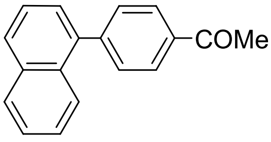
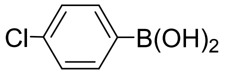
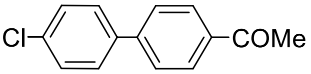
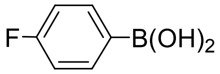
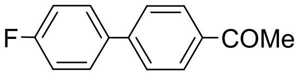
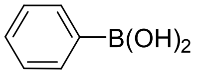
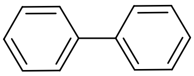
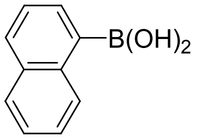
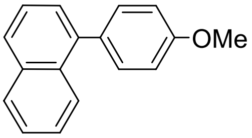
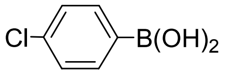
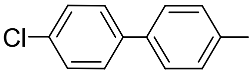
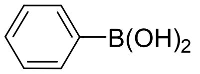
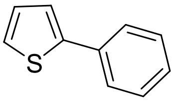
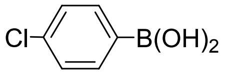
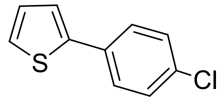
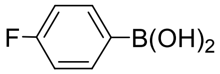
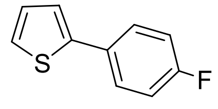
Experimental:

The aryl halide (1mmol), boronic acid (1.2 mmol), K_2CO_3 (1.5 mmol) and 50 mg of Nano-Pine-Pd catalyst were added to 2 mL DMF:H_2O (1:1) in a 10 mL crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. The reaction tube was then placed inside the cavity of a CEM Discover focused MW synthesis system, operated at 100 $\pm$ 5 ^oC (temperature monitored by a built-in infrared sensor), power 200 Watt (maximum), and pressure 50 psi (maximum) for 20 minutes. Gas chromatography (GC) was used to monitor the reactions. The substrate conversions and product selectivities were determined by GC-MS. The crude products were identified by GC-MS qualitative analysis using a GC system with a mass selective detector, by comparing their MS spectra with standard Wiley library. After completion of the reaction, the reaction mixture was decanted to separate nanomaterials and crude product, which was further purified by flash column chromatography (silica gel; ethyl acetate:hexane). The identities were further confirmed for representative compounds by ^1H and ^{13}C NMR spectra that were recorded in deuterated chloroform-*d* ($CDCl_3$) with tetramethylsilane (TMS) as internal reference using a 300 MHz NMR spectrometer. All products (Table 1) are known in the literature and were identified.

Results and Discussion:

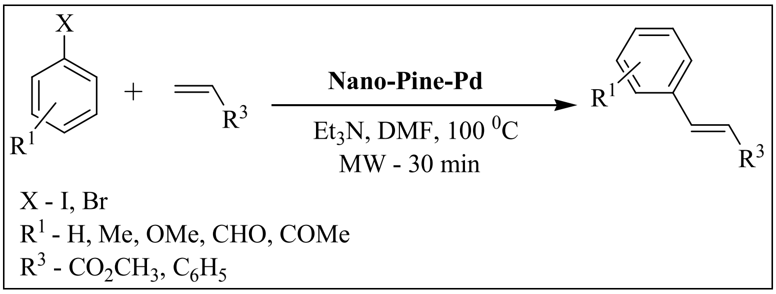
Table 1. Suzuki reaction of various aryl halides using Nano-pine-Pd catalyst.

Entry	Aryl Halide	Boronic Acid	Product	Yield (%)
1	4-OMeC_6H_5Br			96
2	4-OMeC_6H_5Br			95

3	4-CHOC$_6$H$_5$Br			96
4	4-CHOC$_6$H$_5$Br			94
5	4-CHOC$_6$H$_5$Br			94
6	4-COMeC$_6$H$_5$Br			95
7	4-COMeC$_6$H$_5$Br			95
8	4-COMeC$_6$H$_5$Br			95
9	C$_6$H$_5$I			98
10	4-OMeC$_6$H$_5$I			96
11	4-MeC$_6$H$_5$I			96
12	2-Iodothiophene			92
13	2-Iodothiophene			92
14	2-Iodothiophene			94

Aryl bromide (entries 1-8) and aryl iodide (entries 9-14) with various functional groups efficiently reacted with boronic acid to yield Suzuki products in good to excellent yields. 2-Iodothiophene underwent smooth reaction with various boronic acids (entries 12-14), providing a useful way for the synthesis of aryl-substituted thiophene heterocycles.

Heck Reaction:



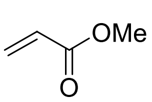
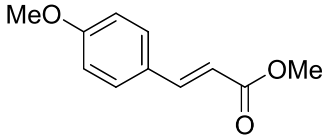
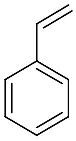
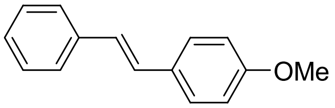
Scheme 2. Heck reaction using Nano-pine-Pd catalyst.

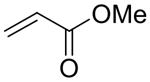
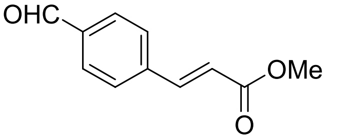
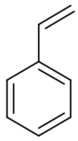
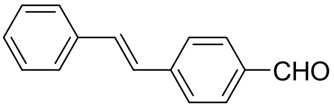
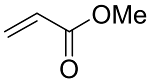
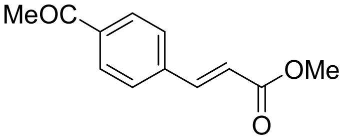
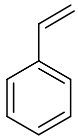
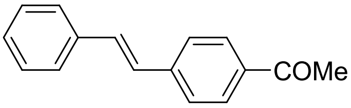
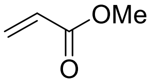
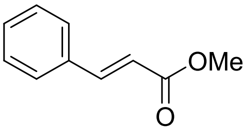
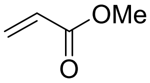
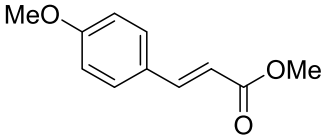
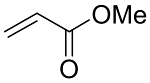
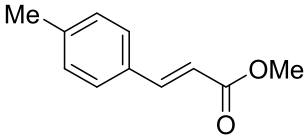
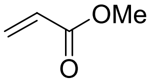
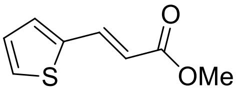
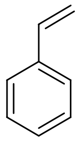
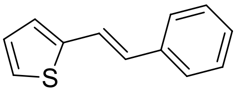
Experimental:

The aryl halide (1mmol), alkene (1.2 mmol), triethylamine (1.5 mmol), and 0.1 g of Nano-pine-Pd catalyst were added to 2 mL DMF in a 10 mL crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. The reaction tube was then placed inside the cavity of a CEM Discover focused MW synthesis system, operated at 100 ± 5 °C (temperature monitored by a built-in infrared sensor), power 200 Watt (maximum), and pressure 80 psi (maximum) for 30 minutes. Gas chromatography (GC) was used to monitor the reactions. The substrate conversions and product selectivities were determined by GC-MS. The crude products were identified by GC-MS qualitative analysis using a GC system with a mass selective detector, by comparing their MS spectra with standard Wiley library. After completion of the reaction, the reaction mixture was decanted to separate nanomaterials and crude product, which was further purified by flash column chromatography (silica gel; ethyl acetate:hexane). The identities were further confirmed for representative compounds by ^1H and ^{13}C NMR spectra that were recorded in deuterated chloroform-*d* ($CDCl_3$) with tetramethylsilane (TMS) as internal reference using a 300 MHz NMR spectrometer.

Results and Discussion:

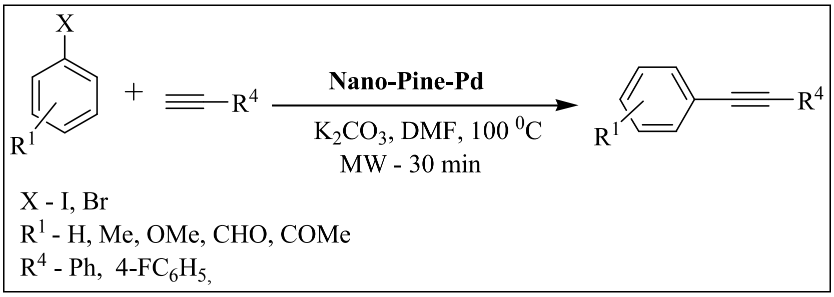
Table 2. Heck reaction of various aryl halides using nano-pine-Pd catalyst.

Entry	Aryl Halide	Alkene	Product	Yield (%)
1	4-OMeC_6H_5Br			87
2	4-OMeC_6H_5Br			88

3	4-CHOC$_6$H$_5$Br			88
4	4-CHOC$_6$H$_5$Br			89
5	4-COMeC$_6$H$_5$Br			85
6	4-COMeC$_6$H$_5$Br			84
7	C$_6$H$_5$I			95
8	4-OMeC$_6$H$_5$I			96
9	4-MeC$_6$H$_5$I			90
10	2-Iodothiophene			90
11	2-Iodothiophene			88

Aryl bromides and iodides reacted efficiently with alkenes to give Heck coupling products in good to excellent yields. The reactions with 2-iodothiophene were successfully achieved (entries 10, 11), which provide a useful strategy to introduce unsaturated group on the thiophene ring.

Sonogashira Reaction:



X - I, Br
R^1 - H, Me, OMe, CHO, COMe
R^4 - Ph, 4-FC_6H_5,

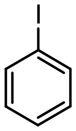
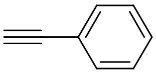
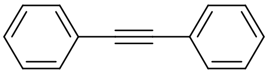
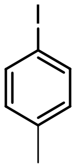
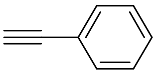
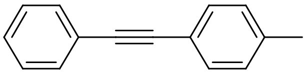
Scheme 3. Sonogashira reaction using Nano-pine-Pd catalyst.

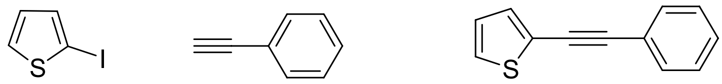
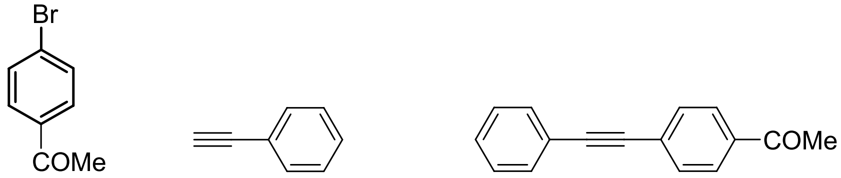
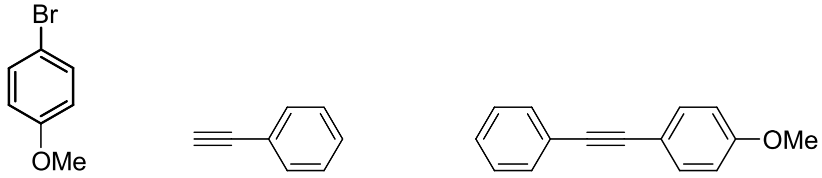
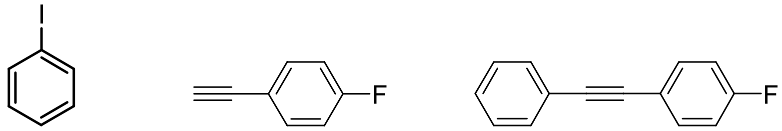
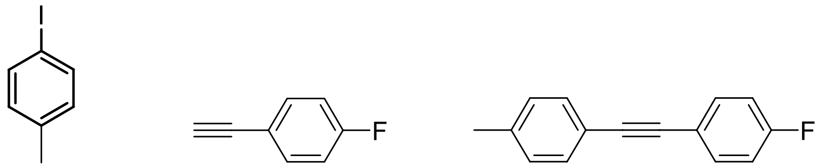
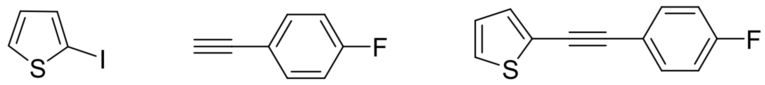
Experimental:

The aryl halide (1mmol), alkyne (1.2 mmol), K_2CO_3 (1.5 mmol), and 0.1 g of Nano-pine-Pd catalyst were added to 2 mL DMF in a 10 mL crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. The reaction tube was then placed inside the cavity of a CEM Discover focused MW synthesis system, operated at 110 ± 5 °C (temperature monitored by a built-in infrared sensor), power 200 Watt (maximum), and pressure 85 psi (maximum) for 45 minutes. Gas chromatography (GC) was used to monitor the reactions. The substrate conversions and product selectivities were determined by GC-MS. The crude products were identified by GC-MS qualitative analysis using a GC system with a mass selective detector, by comparing their MS spectra with standard Wiley library. After completion of the reaction, the reaction mixture was decanted to separate nanomaterials and crude product, which was further purified by flash column chromatography (silica gel; ethyl acetate:hexane). The identities were further confirmed for representative compounds by ^{1}H and ^{13}C NMR spectra that were recorded in deuterated chloroform-*d* ($CDCl_3$) with tetramethylsilane (TMS) as internal reference using a 300 MHz NMR spectrometer.

Results and Discussion:

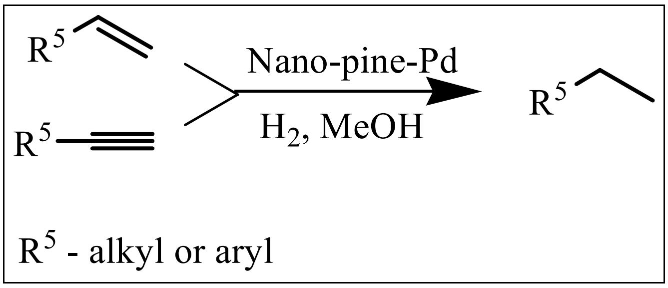
Table 3. Sonogashira reaction of various aryl halides using nano-pine-Pd catalyst

Entry	Aryl Halide	Alkyne	Product	Yield (%)
1				85
2				82

3		79
4		82
5		80
6		88
7		85
8		80
9		84
10		86

Aromatic iodo- and bromo- compounds were efficiently reacted yielding coupling products in good to excellent yields. The reactions with 2-iodothiophene were successfully achieved (Table 3, entry 3), which provide a useful way for introduction of alkyne group on thiophene ring.

Hydrogenation Reaction:



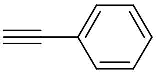
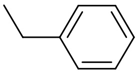
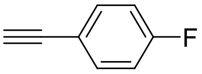
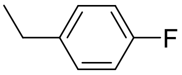
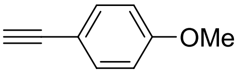
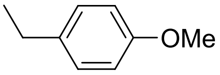
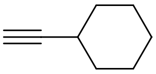
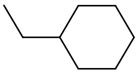
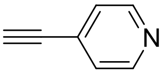
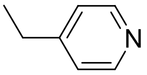
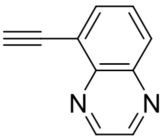
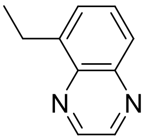
Scheme 3. Hydrogenation reaction using Nano-pine-Pd catalyst.

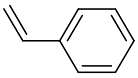
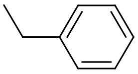
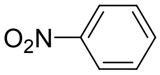
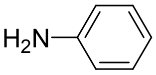
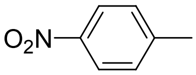
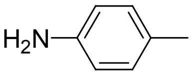
Experimental:

To a solution of alkynes/alkenes/ nitro-compounds (1 mmol) in 2 mL methanol, 10 mg of nano-pine-Pd catalyst was added. The reaction vessel was purged three times with hydrogen and charged to 40 psi, and then closed off to the source of hydrogen. The reaction was stirred for 2 hr at room temperature. After completion of the reaction, the reaction mixture was decanted to separate nanomaterials and crude product, which was further purified by flash column chromatography (silica gel; ethyl acetate:hexane) or distillation.. All products (Table 4) are known in the literature and were identified by comparing their MS spectra with standard Wiley library.

Results and Discussion:

Table 4. Hydrogenation reaction of various alkynes/alkenes/ nitro-compounds using nano-pine-Pd.

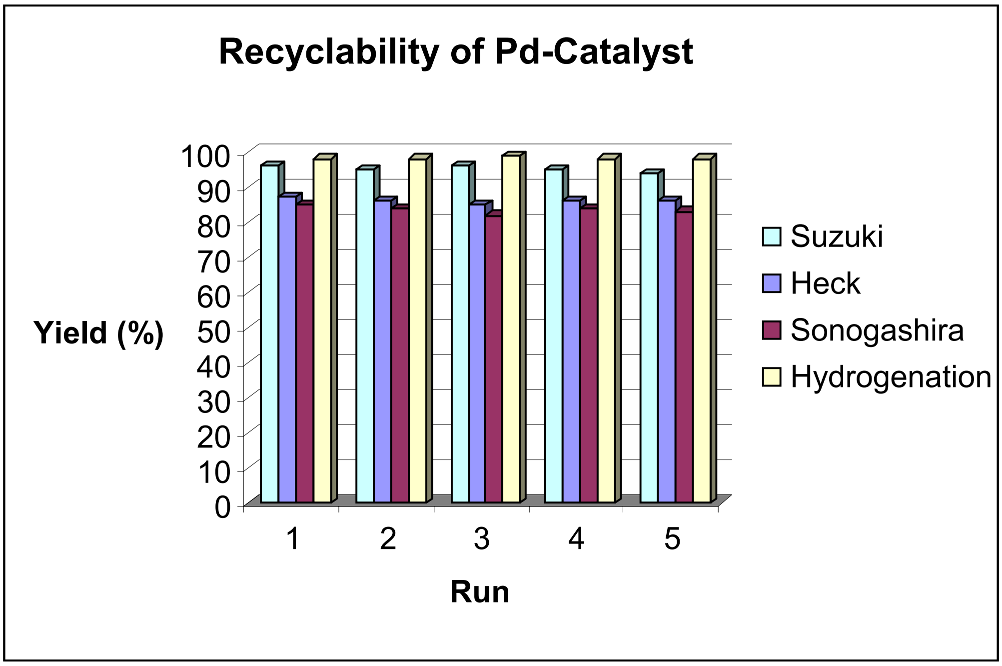
Entry	Substrate	Product	Yield (%)
1			98
2			96
3			96
4			90
5			92
6			94

7			98
8	$CH_3(CH_2)_{11}CH{=}CH_2$	$CH_3(CH_2)_{11}CH_2CH_3$	98
9			97
10			96

The hydrogenation of various unsaturated compounds was explored (Table 4) and each of the reactions described above proceeded smoothly at room temperature to give the desired products. Alkynes were hydrogenated to give yields that were greater than or equal to 90% (entries 1 through 6). Heterocyclic alkynes (entries 5 and 6) can also be reduced in short reaction times to give excellent yields. In addition to alkynes, alkenes can be hydrogenated quickly and in high yield to corresponding alkanes (entries 7 and 8). Lastly, nitro-groups can also be reduced to amine groups with yields greater than or equal to 96 % at room temperature (entries 9 and 10).

Recyclability and Reusability of Pd-Catalyst:

For practical applications of heterogeneous systems, the lifetime of the catalyst and its level of reusability are very important factors. To clarify this issue, we established a set of experiments for the Suzuki reaction of iodobenzne and phenylboronic acid using the nano-pine-Pd catalyst. After the completion of the first reaction to afford the corresponding product, the catalyst was recovered, washed with methanol, and finally dried at 50 ^{0}C. A new reaction was then performed with fresh iodobenzne and phenylboronic under the same conditions. This catalyst could be used at least 5 times without any change in the activity. Similar experiments were also carried out for Heck reaction (substrates - iodobenzene and methyl acrylate); Sonogashira reaction (substrates - iodobenzene and phenyl acetylene); Hydrogenation reaction (substrate - phenyl acetylene). The nano-catalyst showed excellent recyclability in all the reactions and no catalyst deterioration was observed, confirming its high stability.



Pd Leaching Study:

Heterogeneity and metal leaching of this catalyst for the Heck reaction of iodobenzene and methyl acrylate were examined by the modified 'hot filtration' test. The reaction was stopped at 25 % conversion (10 min reaction time). After 1 min, the reaction mixture turned clear liquid and solid catalyst was deposited on the magnetic bar. Half of the liquid reaction mixture was placed into another reaction tube.. After an additional 20 min MW exposure at 100 ^{0}C, the portion containing the nano-catalyst showed 95 % conversion, while the catalyst-free portion showed 30% conversion, evidently proving the heterogeneity of catalyst. Metal leaching was studied by ICP-AES analysis of the catalyst before and after the reaction. The Pd concentration of the catalyst was found to be 7.26 % before the reaction and 7.12 % after the reaction and there was no Pd detected in the final hydration product, which confirmed negligible Pd leaching. This is due to well defined amine-binding sites located on the surfaces of nano-pine-ferrites (Scheme 1), which act as a pseudo-ligands by non-covalent binding with Pd through metal-ligand interactions. This non-covalent anchoring minimizes deterioration and metal leaching and allows efficient catalyst recycling. In fact, to date there is no 100% leach-proof Pd catalyst and the most important criterion in choosing a catalyst is the metal recovery. It would be preferable to use a nano-pine-Pd catalyst, provided that the reaction produces excellent yields and that the catalyst leaves no remnants of metal in the end product, since metal contamination is highly regulated by the pharmaceutical industries. All above conditions were well satisfied by our recyclable nano-pine-Pd catalyst.