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Ultrasmall Pt Stabilized on Triphenylphosphine Modified Silica for Chemoselective Hydrogenation

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Abstract: Chemoselective hydrogenation of substrates bearing more than one functional groups that could be hydrogenated is quite challenging and has fundamental importance. Herein, we report the enhanced chemoselectivity of ultrasmall (< 1 nm) Pt nanoparticles (NPs) stabilized on silica modified with triphenylphosphine (PSiO₂) in hydrogenation reactions. Pt NPs on PSiO₂ exhibits much higher selectivity than those on SiO₂ in the hydrogenation of acetophenone to 1-phenyl ethanol (99.9% versus 36%) and hydrogenation of phenylacetylene to styrene (85% versus 52%). The results of NMR, XPS and in-situ CO adsorption FT-IR spectroscopy indicate the existence of strong interaction among triphenylphosphine and Pt NPs. Consequently, Pt NPs on PSiO₂ has smaller particle size and more positive Pt 4f binding energy than Pt/SiO2, which mainly contribute to the superior chemoselectivity of Pt NPs. We believe that the organically modified silica could act as an efficient solid ligand for tuning the catalytic performance of metal NPs.

Introduction

Chemoselective hydrogenation catalyzed by supported metal nanoparticles (NPs) is an important area of research for sustainable production of fine chemicals.^[1] However, high "chemoselectivity" in hydrogenation is quite challenging with substrates bearing more than one functional groups (C=C, C=O, C=C etc.) that could be easily hydrogenated.^[2] Several approaches have been employed for adjusting the chemoselectivity of hydrogenation reactions, such as by addition of additives, poisoning some of the most active sites of metal NPs, and modifying spacial environment, size and electronic properties of metal NPs.^[3]

In homogeneous catalysis, the utility of organic "ligands" in modifying spatial or electronic properties of metal complexes and/or organometallic intermediates has been a widely used strategy.^[4] However, the tuning of electronic properties of metal NPs by organic ligand is not well investigated in heterogeneous catalysis and is so far limited to a few reports.^[5-7] Zheng and coworkers found that ethylenediamine-coated Pt nanowires show high selectivity for thermodynamically unfavorable N-

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Supporting information for this article is given via a link at the end of

hydroxylanilines.^[5b] Very recently, Glorious and co-workers reported that the chemoslectivity of Ru/K-Al₂O₃ could be greatly enhanced with N-heterocyclic carbene (NHC) as modifier in obtaining partial hydrogenation products of acetophenone, stilbene, and phenylacetylene.^[6] Triphenylphosphine (PPh₃) as a quite popular and versatile ligand in homogenous catalysis has been employed to stabilize Pd, Ru, Ir, Rh, Au NPs and obvious ligand effect on chemoselectivity in partial hydrogenation of substituted arene was observed.^[7] The above work demonstrates that the electron donating and/or withdrawing characteristics of ligands are quite useful in modifying the catalytic performance of metal NPs.

However, organic ligands modified on metal NPs/nanowires may break from the support and/or are generally consumed during the reaction process, which requires continuous addition of ligands to keep stable performance of metal NPs. Also, the ligand-stabilized "soluble" metal NPs face the difficulties in product separation and catalyst recycling. Cross-linking of organic groups on solid supports may partly solve the above problems. Previously, thiol (-SH) functionalized porous polymers and amine (-NH₂) functionalized silica have been employed to stabilize and tune the activity of metal NPs (Au, Pt, and Pd etc.) on account of the promotional effect by thiol and amine groups,^[8] however such investigation has been rarely done with PPh3-functionalized solid supports. Only some nonporous styrene-divinylbenzene copolymers with pendant PPh₃ groups are used for stabilizing Pd, Rh NPs, but the interaction between NPs and PPh3 support has not been thoroughly investigated.^[9]

Herein, we report that the silica modified with high surface area triphenylphosphine polymer ($PSiO_2$) is an efficient solid support for stabilizing ultrasmall Pt NPs for tuning its catalytic performance. Pt NPs supported on $PSiO_2$ exhibits high chemoselectivity for hydrogenation of acetophenone (99.9% sel. to 1-phenylethanol at 100% conv.) and phenylacetylene (87.5% sel. to styrene at 72% conv.). Our preliminary results demonstrate that the silica modified with phosphine polymers are beneficial in controlling the catalytic performances of Pt NPs for the accomplishment of selective hydrogenation reactions.

Results and Discussion

1. Synthesis and Characterization

The hybrid material with PPh₃ cross-linked on silica was prepared by one-pot facile polymerization method as illustrated in Scheme 1. Based on TG analysis, the polymer content on PSiO₂ is *ca.* 25 wt%, corresponding to *ca.* 99% monomer in the initial mixture was cross-linked on silica by polymerization (Figure S1). ICP analysis shows that the PSiO₂ has the P content of 2.34 wt%. The Fourier-transform infrared (FT-IR), ¹³C CP-MAS and ³¹P MAS NMR spectra of PSiO₂ are summarized in Figure 1. In addition to the large and broad peak at 1100 cm⁻¹

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Scheme 1. Schematic illustration for the preparation of PSiO₂ and Pt/PSiO₂ (via AIBN initiated polymerization of tris(4-vinylphenyl)phosphine in the presence of fumed SiO₂) and loading of Pt NPs on PSiO₂.

assigned to -Si-O stretching vibration, the peak at 830 cm⁻¹ for C-P stretching,^[10] 1600 cm⁻¹ for aromatic C=C stretching, and 2923 cm⁻¹ for C-H stretching are observed, which clearly shows the successful incorporation of PPh₃ on the silica. The characteristic carbon peak for C-P appears at 148 ppm along with other aromatic C=C and =C-H bands at 136, 132, 128, 112 ppm and aliphatic CH₂ at 42 ppm.^[10] Additionally, the ³¹P MAS NMR spectrum shows important insights regarding the presence of PPh₃ polymer. The peak at -5.6 ppm corresponds to free phosphorous in tertiary state and the relatively small peak at 25.8 ppm could be assigned to quarternary "P" atom, mainly because of the oxidation of PPh₃ moiety.^[10,11] The combined results of TGA, FT-IR, and NMR confirm the successful modification of silica with cross-linked PPh₃ ligand.

The porous structure of PSiO₂ and SiO₂ were characterized with N₂ adsorption-desorption isotherm (Figure 2) and the physical parameters are summarized in Table 1. The N₂ sorption isotherms of PSiO₂ and SiO₂ show type I isotherm pattern characteristics of microporous materials. The sharp N₂ uptake at P/P₀ (~0.9) suggests the existence of intervoid space due to particle aggregation. The N₂ uptake at P/P₀ (<0.1) is sharper in PSiO₂ than that in SiO₂, signifying that PSiO₂ has more amount of microporous than SiO₂. The previous study suggests that the polymerization of PPh₃ containing precursor results in the formation of microporous polymers.^[11-12]

Consequently, the BET surface area, pore volume and micropore volume of $PSiO_2$ are higher than SiO_2 . The N_2 sorption results further confirm the existence of PPh_3 polymer on $PSiO_2$.

Pt NPs were loaded onto $PSiO_2$ through impregnationreduction method. Compared with $PSiO_2$, slight decrease in BET surface area and micropore volume were observed with Pt/PSiO₂ (Table 1). Similar tendency was also observed for Pt/SiO₂. The FT-IR spectrum of Pt/PSiO₂ is almost identical to that of PSiO₂, indicating that Pt loading did not disturb the composition of PSiO₂ (Figure 1a).

HAAD STEM technique was used to characterize the particle size of Pt on Pt/PSiO₂ and Pt/SiO₂ (Figure 3). The STEM image of Pt/SiO₂ clearly shows that Pt NPs have average size of 1-3 nm but for Pt/PSiO₂, it is hard to clearly estimate the particle size of Pt NPs from STEM due to the poor conductivity of the sample (possibly because of the existence of thick polymers). However, existence of Pt NPs with particle size less than 1 nm could still be observed from HAAD STEM image of Pt/PSiO₂. The formation of small Pt clusters on Pt/PSiO₂ is possibly due to the coordination ability of phosphorous ligand to Pt NPs. The formation of ultrasmall metal NPs, especially for noble metals, is difficult but quite important to improve the usage efficiency of expensive metal nanoparticles.



Figure 1. (a) FT-IR spectra of PSiO₂ and Pt/PSiO₂, (b) ¹³C CP-MAS NMR spectrum of PSiO₂ and (c) ³¹P MAS NMR spectra of PSiO₂ and Pt/PSiO₂ (*indicates spinning side bands)



Figure 2. N₂ adsorption (open circles and triangles), desorption (closed circles and triangles) isotherms of SiO₂ and PSiO₂ respectively.

Table 1. Physical and chemical parameters of $PSiO_2$ and SiO_2						
Sample	S _{BET} ^[a] (m ² g ⁻¹)	S _{micro} (m ² g ⁻¹)	V _{total} ^[b] (cm ³ g ⁻¹)	P (wt%)	Pt ^[c] (wt%)	Pt ^[d] (nm)
PSiO ₂	490	45	1.7	2.3	-	-
SiO ₂	215	17	0.6	-	-	-
Pt/PSiO ₂	478	38	1.5	2.3	1.65	< 1
Pt/SiO ₂	167	-	0.7	-	0.50	1-3

[a]BET surface area was measured from N₂ sorption isotherm at 77 K; [b]Total pore volume was measured at $P/P_0 = 0.98$; [c]measured from ICP analysis; [d] Pt size distribution from STEM analysis.

catalyzed by solid catalyst and no leaching of Pt occurs during the catalytic process (Figure 4a).



2. Chemoselective hydrogenation

Hydrogenation of acetophenone could produce 1-phenyl ethanol (A), 1-cyclohexyl ethanone (B), and 1-cyclohexyl ethanol (C), as shown in Table 2.^[13] With Pt/SiO₂ as catalyst, the selectivity to desired product, 1-phenyl ethanol, is only 36% at conversion of 17% and the main product is fully hydrogenated 1-cyclohexyl ethanol. Commercial Pt/C gives selectivity to A of 63.5% with conversion of 92%. This suggests that PtSiO₂ and Pt/C has very poor chemoselectivity.

Under similar reaction conditions, Pt/PSiO₂ could obtain >99.9% selectivity to A with conversion of 100%, suggesting that carbonyl bond is preferred for hydrogenation. The control sample, H₂PtCl₆/PSiO₂ (prepared by impregnation of H₂PtCl₆ on PSiO₂ without reduction) shows no activity in acetophenone hydrogenation reaction, suggesting that Pt NPs are the active sites for this reaction. The kinetic curve of Pt/PSiO₂ indicates that the reaction rate is fast in the initial 20 min without any induction time (Figure 4a). Within 2 h, 100% conversion has been achieved. Hot filtration test was also performed by separation of Pt/PSiO₂ from the reaction system and the filtrate was further subjected for reaction. After 80 minutes no further increase in acetophenone conversion could be found. demonstrating that the hydrogenation reaction is indeed Figure 3. (a) HAAD STEM image of Pt/SiO2 and (b) Pt/PSiO2

Importantly, Pt/PSiO₂ retains high chemoselectivity to 1phenylethanol all throughout the reaction process. Under more harsh conditions, e.g. higher pressure, higher temperature and higher Substrate/Catalyst ratio (S/C), the selectivity to 1-phenyl ethanol maintains as high as 99% (Table 2, Figure 4b). The above results signify that Pt/PSiO₂ has high selectivity to carbonyl hydrogenation even under harsh reaction conditions. Under solvent free conditions, Pt/PSiO₂ could also smoothly catalyze acetophenone hydrogenation reaction to afford turnover frequency (TOF) of 2304 h⁻¹ and selectivity to 1-phenyl ethanol of 99.5%. The H₂ pressure has no influence on the selectivity to 1-phenyl ethanol but affects the activity of Pt/PSiO₂.

The TOF of Pt/PSiO₂ and H₂ pressure follows the volcano curve. During the catalytic process, the H₂ dissociates on Pt NPs and dissociated H reacts with substrates for the formation of product.^[14] Thus the TOF increases with H₂ pressure. However, too much H₂ may inhibit the adsorption of acetophenone on Pt. Consequently, the TOF decreases at high H₂ pressure. When comparing with Pt/C and Pt/SiO₂, Pt/PSiO₂ shows both higher selectivity and higher activity, signifying the superior performance of Pt/PSiO₂.

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Figure 4. (a) Reaction kinetics for Pt/PSiO₂ (ethanol as solvent), (b) Selectivity and TOF of acetophenone hydrogenation to 1-phenyl ethanol on Pt/PSiO₂ at various H_2 pressure considering S/C = 200.

The catalytic performance of Pt/PSiO₂ was also tested in the hydrogenation of phenylacetylene (PA) to styrene because styrene or substituted styrene derivatives are important intermediate/partial hydrogenation product of PA or alkylphenylacetylene, which is difficult to isolate but it has much importance in industry (Table 3). In this regard, high chemoselective synthesis of styrene without formation of undesired ethylbenzene could be scientifically challenging.^[15] Although Pt/PSiO₂ and Pt/SiO₂ could smoothly catalyze this reaction, but the selectivity to styrene is lower (52%) on Pt/SiO₂ in contrast to Pt/PSiO₂ (85.2%) for almost similar conv. of PA. The low styrene selectivity of Pt/SiO₂ could be attributed to its high hydrogenation activity than Pt/PSiO₂, as evidenced that Pt/SiO₂ shows 92% conv. of PA within 20 min. On the other hand, PPh₃ modified catalyst shows relatively sluggish hydrogenation of PA and at 72% conv. of PA, highest styrene selectivity (87.5%) can be achieved after 120 min reaction. This result suggests that Pt/SiO₂ has faster hydrogenation activity and relatively lower selectivity than Pt/PSiO2. Also initial TOF of Pt/SiO₂ is almost 5 times higher that of Pt/PSiO₂, signifying the remarkable effect of phosphor ligands in controlling the catalytic performance of Pt NPs.



[a]Reactions were carried out at 45 °C, 20 bar H₂, phenyl acetylene (50 mg), S/C = 1000; [b]Initial TOF was calculated at 10 min reaction.

The recycle stability of $Pt/PSiO_2$ was also investigated. As shown in Figure 5, both conversion and selectivity did not exhibit any considerable decrease in comparison with the fresh catalyst, demonstrating that $Pt/PSiO_2$ is highly stable and durable.

The acetophenone hydrogenation results show that $Pt/PSiO_2$ is highly chemoselective to partial hydrogenation products such as 1-phenylethanol. This demonstrates the unique role of phosphor ligand in modifying the catalytic performance of Pt NPs. For understanding the influence of PPh₃ ligand on catalytic performance of Pt NPs, ³¹P MAS NMR was firstly employed for characterizing the interaction between Pt NPs and PPh₃ ligand (Figure 1c). For Pt/PSiO₂, the peak with chemical shift at -5.6 ppm assigned to free tertiary phosphorus-

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Figure 5. Recycling stability of Pt/PSiO_2 for acetophenone hydrogenation under solvent free condition at 20 bar H_2, 120 min reaction time, 100 °C, S/C=1000.

-atom decreases in intensity, accompanying by an increase in peak intensity with chemical shift at 28.5 ppm assigned to the phosphorous atom coordinated with Pt NPs. This shows the existence of strong interaction of Pt NPs with PPh₃.

Furthermore, XPS analysis of Pt/PSiO₂ was used to probe the chemical valence state of Pt, which is summarized in Figure 6 and compared with that of Pt/SiO₂ and H₂PtCl₆/PSiO₂. For H₂PtCl₆/PSiO₂, the binding energy (BE) of Pt4f_{7/2} and Pt4f_{5/2} appears respectively at 72.6 eV and 75.9 eV, which is consistent with Pt(IV) as observed in several Pt complexes.^[16] While Pt/SiO₂ gives Pt4f_{7/2} BE at 70.8 eV and Pt4f_{5/2} BE at 74.2 eV, which could be assigned to Pt(0) NPs.^[17] However, Pt4f BE for Pt/PSiO₂ falls at 72.1 eV (4f_{7/2}) and 75.5 eV (4f_{5/2}). Therefore, Pt on PSiO₂ shows positive binding energy shift (+1.28 eV) compared with Pt on silica. This is possibly due to the strong interaction of Pt NPs with organophosphor ligands and also the ultrasmall particle size of Pt NPs, as previously reported.^[18]



Figure 6. XPS spectra of Pt 4f electrons of Pt/SiO_2 (black), $H_2PtCI_6/PSiO_2$ (blue) and $Pt/PSiO_2$ (brown)



Figure 7. In-situ CO adsorption FT-IR spectra of $Pt/PSiO_2$ (red line), Pt/SiO_2 (black line), $H_2PtCl_6/PSiO_2$ (blue line).

For understanding the difference in Pt NPs on SiO₂ and on PSiO₂, we measured in-situ CO adsorption FT-IR of Pt/SiO₂ and Pt/PSiO₂ because the stretching frequency of CO is very sensitive to the electronic structure of the metal surface onto which it is chemisorbed (Figure 7).^[19] In-situ CO adsorption FT-IR spectrum of Pt/SiO₂ clearly shows CO adsorption band at 2083 cm⁻¹ corresponding to linear bound signal for CO. However the band is slightly broad due to strong dipolar coupling interaction between Pt and CO.^[20] Interestingly, no bridging CO adsorption signal was observed in Pt/SiO₂. On the other hand, H₂PtCl₆/PSiO₂ did not show any characteristics CO adsorption signal. Pt/PSiO₂ shows distinguishable and broad CO band at 2081 cm⁻¹, 2019 cm⁻¹, and 1968 cm⁻¹, further confirming the existence of Pt(0) on Pt/PSiO₂. The band at 2081 cm⁻¹ and 2019 cm⁻¹ could be assigned to linearly adsorbed CO on Pt/PSiO₂. It is evident that there are two types of CO linearly adsorbed for Pt/PSiO₂, indicating the presence of two different adsorption sites, Pt(0) and PtPPh₃(0). For Pt/PSiO₂, the additional band at 1968 cm⁻¹ may be assigned to the bridging bound signal of CO, which is responsible to several multimetallic carbonyl complexes.^[21] Interestingly for Pt/PSiO₂, the IR band at 2019 cm⁻ ¹ red shifts from that of Pt/SiO₂ (2083 cm⁻¹). It is worthy to mention, red shift in CO adsorption is responsible to electron rich Pt surfaces, which is justified from the interaction between ultrasmall Pt NPs and basic PPh3 sites.^[22] Therefore from in-situ CO adsorption studies it is clear that Pt/PSiO₂ has at least two types of CO binding site, that is Pt without direct interaction with PPh₃P and Pt directly coordinated with PPh₃P.

Based on NMR, XPS and in-situ CO adsorption FT-IR characterizations, we could see that there are strong interactions among PPh₃ ligand and Pt NPs, which may change the electronic properties of Pt NPs and also results in the formation of ultrasmall Pt NPs. These alterations make Pt/PSiO₂ to exhibit unique chemoselectivity in hydrogenation reactions.

Conclusions

In summary, the tuning of chemoselectivity of Pt NPs was achieved by using silica modified with cross-linked PPh₃ ligand. The PPh₃ ligand not only stabilizes the ultrasmall Pt NPs but also forms strong interaction with Pt NPs. In the hydrogenation of acetophenone and phenylacetylene, Pt/PSiO₂ shows superior chemoselectivity to Pt/SiO₂, which could be attributed to the ligand effect of PPh₃. The solid support modified with organic ligand therefore provides a new approach for tailoring the catalytic performance of metal NPs.

Experimental Section

Chemicals and reagents

All reagents were of analytical grade and used as received unless otherwise stated. H₂PtCl₆ was purchased from Sigma-Aldrich Company, Ltd. (USA). Fumed silica (specification, 7-40 nm size) was obtained from Aladdin-reagent Company, China. Tris(4-vinylphenyl)phosphine was prepared according to the literature report as mentioned elsewhere.^[10] Acetophenone, sodium borohydride, Pt/C (1 wt%) and all other chemicals as required for catalysis were bought from Aladdin-reagent Company, China.

Instrumentation

 N_2 adsorption-desorption isotherm at -196 $^{\circ}\text{C}$ has been measured from Micromeritics ASAP2020 adsorption analyzer with the samples degassed at 100 °C for 6 h. X-ray photoelectron spectroscopy (XPS) was recorded on a VG ESCALAB MK2 apparatus by using AlK α (h λ = 1486.6 eV) as the excitation light source. HAAD STEM has been performed on JEOL JEM ARM200F instrument. Thermogravimetry analysis (TGA) was measured by using a NETZSCH STA 449F3 analyzer from 30 °C to 900 °C with a heating rate of 10 °C min-1 in air. Solid state ³¹P NMR was carried out at 9.4 T on a Varian Infinity Plus 400 spectrometer with a ³¹P frequency of 161.83 MHz using a 5 mm Chemagnetic probe. The chemical shifts were referenced to (NH₄)₂HPO₄. Solid state ¹³C NMR spectra were obtained with a Bruker 500 MHz spectrometer equipped with a magic-angle spin probe using a 4 mm ZrO₂ rotor. $^{13}\!C$ signals were referenced to glycine (C₂H₅NO₂). The experimental parameters were as follows: 8 kHz spin rate, 5 s pulse delay, and 2500 scans. ¹H liquid NMR of the products were measured from Bruker Avance^{III} 400 MHz instrument. Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet Nexus 470 IR spectrometer (KBr pellets were prepared). ICP elemental analysis was performed on PLASAMSPEC-II inductively coupled plasma atomic emission spectrometry (ICP-AES). CO adsorption FT-IR was measured by Nicolot iS50 FT-IR Spectrometer, Thermo Fisher Scientific at 25 °C.

Methods

Synthesis of PSiO₂

Funed silica (1 g) in a round bottom flask was degassed at 120 °C for 3 h. After cooling to room temperature (25 °C) under Ar flow, 40 mL of anhydrous THF was added. Then, tris(4-vinylphenyl)phosphine (PPh₃V, 0.37 g; 1.08 mmol) and azobisisobutyronitrile (AIBN) (3 wt% with respect to PPh₃V) were added to the suspension of silica. The resulting mixture was refluxed at 67 °C for 24 h under Ar atmosphere. Finally, the solid product was filtered and thoroughly washed with THF, ethanol and dried

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under vacuum at room temperature (25 $^{\circ}\text{C}).$ The material was denoted as PSiO2.

Loading of Pt on PSiO₂

PSiO₂ (0.2 g) was dispersed in THF (1.5 mL), followed by the addition of 208 μ L of H₂PtCl₆ solution (0.1 M). After the mixture was stirred for 6 h at 25 °C, the solid material was filtered, washed with water and dried under vacuum. The solid was re-dispersed in deionized water (2 mL), followed by the addition of NaBH₄ (20 equiv with respect to Pt). The suspension was again stirred for 15 h at 25 °C under Ar and thereafter filtered, washed with water, ethanol and dried under vacuum. The black solid was denoted as Pt/PSiO₂, where Pt loading is 2 wt%. For comparison, Pt/SiO₂ with Pt loading of 1 wt% was prepared in a similar method to Pt/PSiO₂ with the exception that fumed silica was used instead of PSiO₂. A control sample H₂PtCl₆/PSiO₂ was prepared in a similar method to Pt/PSiO₂ with the exception that no reduction of Pt complex was done.

Hydrogenation reactions

Hydrogenation of acetophenone

A desired amount of catalyst (12.3 mg, 0.5 mol% Pt; 1.04 x 10⁻⁶ mmol) was added to an ampoule tube, followed by the addition of acetophenone (25 mg, 2.08×10^{-4} mol) and ethanol (2 mL). The ampoule tube was then transferred into a stainless-steel autoclave and sealed, flushed with H₂ three times to remove air from inside the autoclave and finally pressurized to 2 MPa H₂, which was then heated in an oil bath at 60 °C under stirring. After 2 h, the remaining H₂ was carefully discharged and the solid catalyst was separated by centrifugation, the filtrate was collected, diluted with ethanol, and analyzed by using an Agilent 7890 GC instrument equipped with an Agilent J&W GC HP-5 capillary column (30 m x 0.32 mm x 0.25 mm). The products are also characterized by ¹H NMR measurement, as given in Figure S2.

The solvent free reaction was carried out according to the similar procedure as mentioned above, except that 100 °C, Pt/PSiO₂ (6.15 mg, 0.1 mol% Pt; 5.2 x 10^{-7} mmol) and acetophenone (62.5 mg, 5.2 x 10^{-4} mol) was used.

Hydrogenation of phenylacetylene

The catalyst (5 mg, 4.23 x 10^{-7} mmol Pt) was added to an ampoule tube, along with phenyl acetylene (50 mg; 0.5 mmol) without any solvent. The tube was then transferred into a stainless-steel autoclave and sealed, flushed with H₂ three times to remove air from inside the autoclave and finally pressurized to 2 MPa H₂, which was then heated in an oil bath at 45 °C under stirring. The remaining procedure is exactly similar as mentioned for the hydrogenation of acetophenone. In Figure S3 we have given the characterization of products by ¹H NMR.

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