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Silica supported palladium phosphine as a robust and recyclable catalyst for semi-hydrogenation of alkynes using syngas

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ABSTRACT

This work reports a chemo-selective semi-hydrogenation of alkynes to alkenes using silica supported palladium phosphine catalyst with syngas (CO/H_2). This developed methodology is an alternative to classical Lindlar catalyst for chemo-selective semi-hydrogenation of alkynes to alkenes. Various alkynes were smoothly convert to alkenes in 60–97% conversion with 85–98% selectivity. The prepared catalyst was well characterized by Field Emmission Gun Scanning Electron Microscopy (FEG-SEM), Energy Dispersive X-ray Spectroscopy (EDS), X-ray Photoelectron Spectroscopy (XPS), Inductively Coupled Plasma- Atomic Emmission Spectroscopy (ICP-AES) analysis techniques. In addition, catalyst was effectively recycled up to four consecutive run without significant loss in its catalytic activity and selectivity.

1. Introduction

The synthesis of alkenes via chemo-selective semi-hydrogenation of alkynes is an important transformation in the organic synthesis [1,2]. Alkenes are essential intermediates in the pharmaceutical drug moieties, natural products and biological active compounds [3–5]. The styrene derivatives obtained by semi-hydrogenation of phenylacetylene plays an important role in the synthesis of essential monomer of polystyrenes, synthetic rubbers and the various organic commodities [6]. In addition, olefins are also one of the most important starting material for various reactions such as Markovnikoffs addition, epoxidation, ozonolysis, hydroboration, hydrogenation, hydroformylation reactions, etc. [7–9]. The literature survey showed that, various homogeneous catalytic systems were reported for the semi-hydrogenation of terminal alkynes [10]. The first chemical reaction of semi-hydrogenation of alkynes was reported by Heck in 1978 by using Pd/C with tri-alkyl-ammonium formate as a hydrogen source [11,12]. Moreover, the various catalysts has been reported for the conversion of alkynes into alkenes such as, Pd [13–18], Ni [19], Rh [20,21], Ir [22] and Ru [23]. Despite the potential utility of Lindlar catalyst ($Pd/CaCO_3$) treated with $Pb(OAc)_2$) suffers from drawbacks such as use of poisonous lead (Pb) salt and excess use of quinoline to control the over hydrogenation, which limits in the substrate scope and selectivity [24]. Heterogeneous catalysis based on Pd and Ni metals has extensively studied for reduction of alkynes to *Z*-alkenes using H_2 as a reducing source, but it suffers from the over reduction of alkenes [25–27]. In recent times, heterogeneous Palladium (Pd), Platinum (Pt) and Iron (Fe) catalyst are reported for selective hydrogenation/dehydrogenation reactions [28–30].

Recently, Wagh et al. reported the transfer semi-hydrogenation of alkynes by using heterogeneous gold catalyst with $HCOOH/NEt_3$. In this method, HCOOH served as a hydrogen source and NEt_3 as an additive [31]. Alternatively, the number of lead-free catalytic systems have been reported for semi-hydrogenation of alkynes in literature [32–47]. Takahashi et al. also reported that lead free catalytic system for the selective semi-hydrogenation of alkynes by using silica supported Pd nanoparticles (PdNPs) with dimethylsulfoxide (DMSO) as an additive [48]. Considering all above the environmental issues, the development of the simple catalytic systems, additive free, co-catalyst free protocol is highly desirable.

The syngas is commercially produced by steam reforming or partial oxidation technology of natural gas. It is extensively used for the synthesis of ammonia, methanol, hydrogen and other impor-

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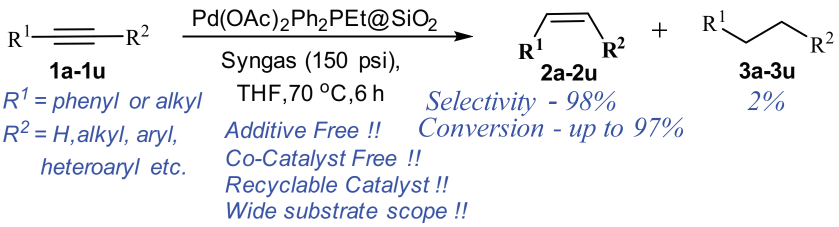


Scheme 1. The semi-hydrogenation of terminal and internal alkynes.

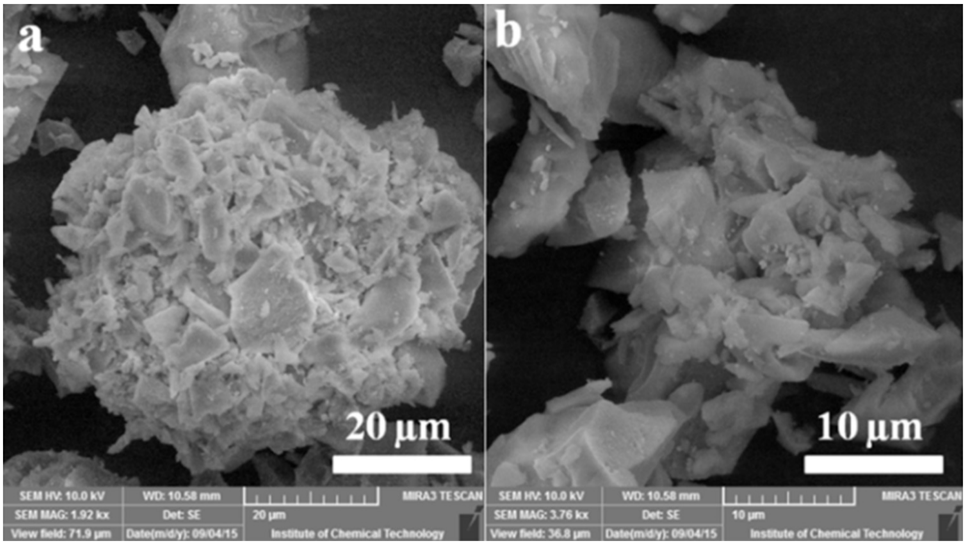


Fig. 1. FEG-SEM images of $Pd(OAc)_2Ph_2PEt@SiO_2$ fresh catalyst before the reaction.

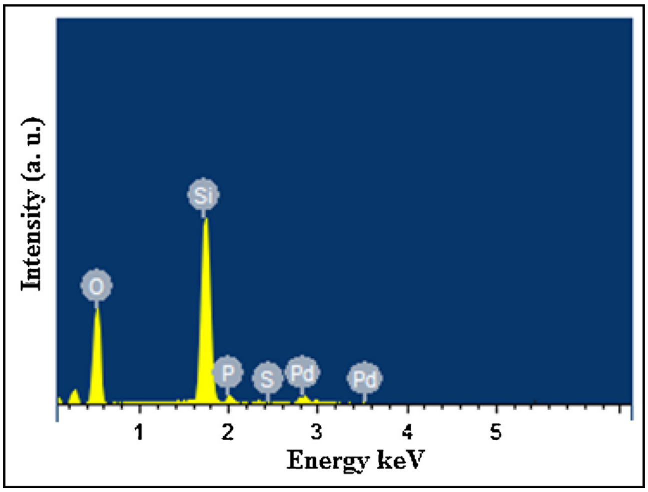


Fig. 2. EDS image of fresh $Pd(OAc)_2Ph_2PEt@SiO_2$ catalyst.

tant products in the industries [49]. Generally, the syngas is widely used in the well known hydroformylation reaction for the conversion of olefins to aldehydes [50–53]. Takahashi et al. disclosed the use of syngas for the hydrogenation of aldehydes to alcohols by using ruthenium as a catalyst [54]. However, the important class of semi-hydrogenation reactions has not yet been reported using syngas as hydrogen source.

Herein, we first time report the use of syngas as hydrogen source for the selective semi-hydrogenation of alkynes to alkenes using silica-supported palladium-phosphine as a heterogeneous catalyst (Scheme 1). The developed method tolerates wide range of internal as well as terminal alkynes which affords the respective alkenes with 85–98% selectivity.

2. Experimental

2.1. Materials and methods

All the reactions were performed in inert conditions under the nitrogen atmosphere by using 100 mL stainless steel high pressure reactor. All the chemicals and reagents were purchased form Sigma Aldrich, S.D. Fine and commercial suppliers. The solvents were purchased from commercial suppliers and used without further purification. The prepared $Pd(OAc)_2PPh_2Et@SiO_2$ catalyst was well characterized by using FEG-SEM, EDS, XPS and ICP-AES spectroscopic analysis techniques. The loading of catalyst was calculated by XRF measurements (SEA-2010, Seiko Electronic Industrial Co., Japan). The XPS of $Pd(OAc)_2PPh_2Et@SiO_2$ was measured using a PHI5000 Versa Probe with a monochromatic focused (100 µm × 100 µm) Al Kα X-ray radiation (15 kV, 30 mA) and dual beam neutralization using a combination of Argon ion gun and electron irradiation. Reaction monitor by using PerkinElmer Clarus 400 gas chromatography equipped with flame ionization detector with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 µm). GC-MS-QP 2010 instrument (Rtx-17, 30 m × F5 mm ID, film thickness (df) = 0.25 µm) was used for the mass analysis of the products. Products were purified by column chromatography on silica (120–200 mesh). Nuclear magnetic resonance spectra were taken on Bruker in $CDCl_3$ solvent (^1H, 400 MHz; ^{13}C, 100 MHz) spectrometer using tetramethylsilane (1H) as an internal standard. The chemical shifts values are reported in parts per million (δ) relative to tetramethylsilane as an internal standard. The J (coupling con-

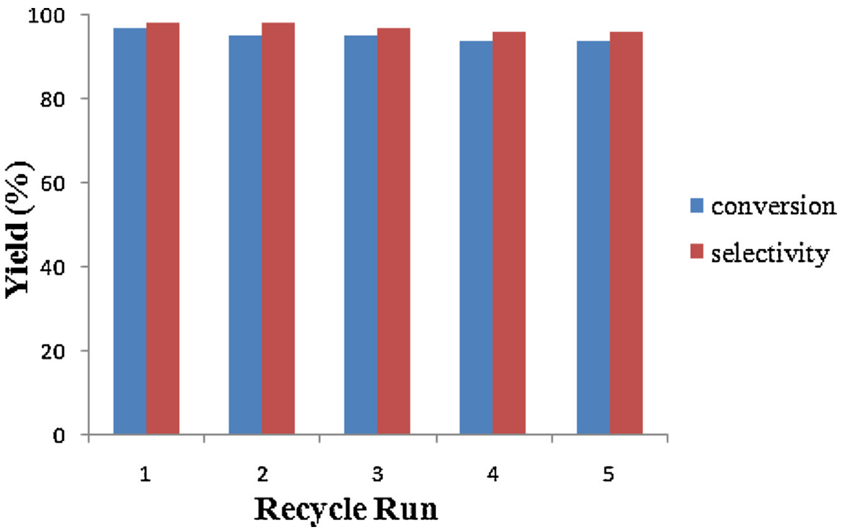


Fig. 3. Recyclability study of the $Pd(OAc)_2PPh_2Et@SiO_2$ catalyst.

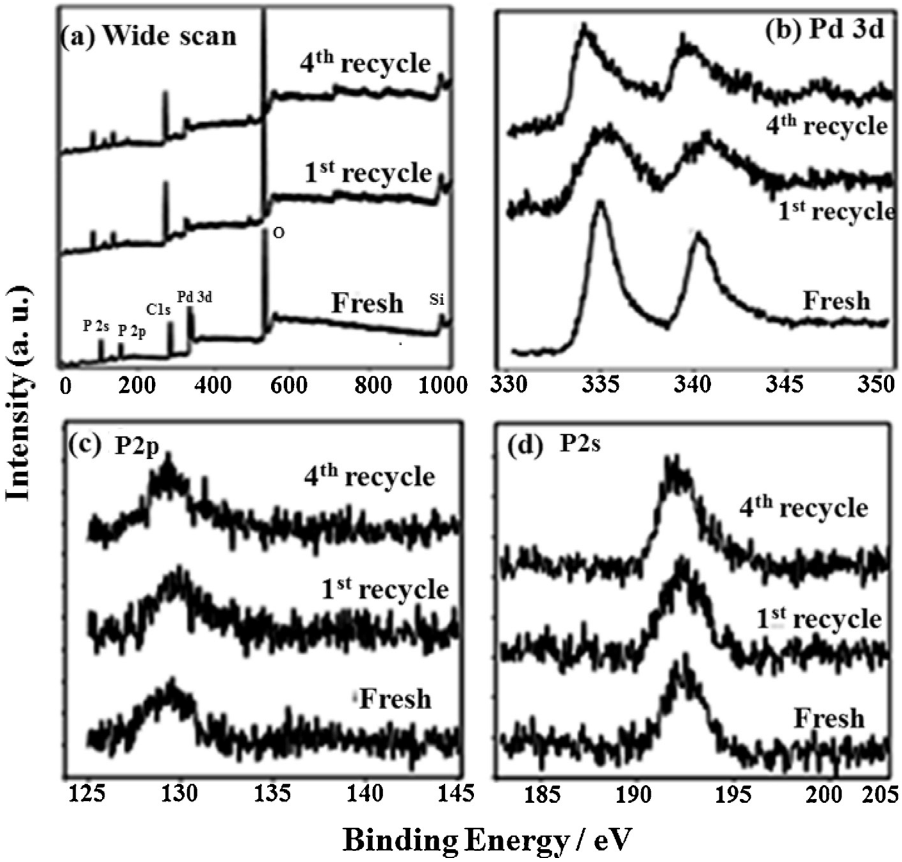


Fig. 4. XPS images of the $Pd(OAc)_2PPh_2Et@SiO_2$ catalyst (a) wide scan, (b) Pd 3d region, (c) P2p region, (d) P2s region.

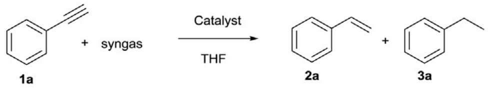
stant) values were described in Hz. Splitting patterns of proton are depicted as s (singlet), d (doublet), t (triplet) and m (multiplet). The products were confirmed by the comparison of their GC, GC-MS, ^{1}H and ^{13}C NMR spectra with those of authentic data.

2.2. Synthesis and characterization of the catalyst

2.2.1. Synthesis of silica supported $Pd(OAc)_2PPh_2Et$ catalyst

The procedure for the silica supported $Pd(OAc)_2PPh_2Et$ catalyst is: in a 100 mL round bottom flask 0.472 g of $Pd(OAc)_2$ and 3.0 g of PPh_2Et/SiO_2 (2-diphenylphosphinoethyl functionalized silica, 0.7 mmol/g) acquired from Aldrich were mixed properly, stirred and refluxed with acetonitrile under nitrogen atmosphere for 48 h. The material showing black was filtered with 0.45 μm PTFE filter and washed several times with acetonitrile then dried at room temperature. The metal loading of $Pd(OAc)_2PPh_2Et@SiO_2$ was 6.4 wt% as determined by XRF measurements (SEA-2010, Seiko Electronic Industrial Co., Japan).

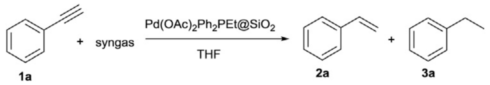
Table 1
The study of catalyst screening and loading for semi-hydrogenation of Phenyl acetylene (**1a**) to styrene (**2a**).[a]



Entry	Catalyst	Catalyst loading (mol%)	Conversion of **1a** (%)[a]	Selectivity of **2a**/**3a** (%)[b]
1	$Pd(OAc)_2$	0.50	80	85/15
2	$PdCl_2(PPh_3)_2$	0.50	40	90/10
3	$Pd(OAc)_2Ph_2PEt@SiO_2$	1.28	98	92/08
4	Pd/C (10%)	3.00	90	88/12
5	$PdBr_2$	1.20	67	76/24
6	$Pd(OAc)_2Ph_2PEt@SiO_2$	0.50	90	92/08
7	$Pd(OAc)_2Ph_2PEt@SiO_2$	0.64	95	95/05
8	$Pd(OAc)_2Ph_2PEt@SiO_2$	0.96	97	98/02
9	$Pd(OAc)_2Ph_2PEt@SiO_2$	1.60	99	90/10
10	$Pd(OAc)_2Ph_2PEt@SiO_2$	1.92	100	82/18
11	No catalyst	–	–	–/–

[a] Reaction Conditions: 1a (1 mmol), syngas (150 psi), THF (10 mL), temp. (80 °C), time (8 h).
[b] GC Yield.

Table 2
Optimization study of semi-hydrogenation of phenyl acetylene (**1a**).[a]



Entry	CO/H_2 (psi)	Time (h)	Temperature (°C)	Solvent	Conversion of **1a** (%)[a]	Selectivity of **2a**/**3a** (%)[b]
Effect of syngas pressure						
1	1/1(300)	10	80	THF	82	89/11
2	1/1(200)	10	80	THF	85	95/05
3	1/1(150)	10	80	THF	98	97/03
4	1/1(100)	10	80	THF	94	92/08
5	2/1(150)	10	80	THF	60	71/29
6	1/2(150)	10	80	THF	91	79/21
7[c]	1/0(150)	10	80	THF	–	–/–
8[d]	0/1(150)	10	80	THF	100	–/100
Effect of time						
9	1/1(150)	8	80	THF	97	97/03
10	1/1(150)	6	80	THF	97	98/02
11	1/1(150)	4	80	THF	94	97/03
Effect of temperature						
12	1/1(150)	6	60	THF	92	95/05
13	1/1(150)	6	70	THF	97	98/02
14	1/1(150)	6	90	THF	98	90/10
15	1/1(150)	6	100	THF	100	85/15
Effect of solvent						
16	1/1(150)	6	70	1,4 Dioxane	99	85/15
17	1/1(150)	6	70	EtOH	89	92/08
18	1/1(150)	6	70	MeOH	86	89/11
19	1/1(150)	6	70	Toluene	79	90/10
20	1/1(150)	6	70	DMF	92	94/06

[a] Reaction Conditions: 1a (1 mmol), solvent (10 mL), Pd catalyst (0.96 mol%), 400 rpm.
[b] GC Yield.
[c] Reaction under CO atm.
[d] Reaction under H_2 atm.

2.2.2. Characterization of prepared silica supported $Pd(OAc)_2PPh_2Et$ catalyst

The silica supported $Pd(OAc)_2PPh_2Et$ catalyst was characterized by FEG-SEM, EDS, XPS, ICP-AES analysis techniques. The morphology of the samples was examined using field emission gun-scanning electron microscopy (FEG-SEM) analysis (Tescan MIRA 3 model). The FEG-SEM analysis shows the surface morphology of the material. The as synthesized fresh $Pd(OAc)_2Ph_2PEt@SiO_2$ catalyst shows the flakes like surface morphology. The FEG-SEM images (Fig. 1) display the presence of rough surface of catalyst indicating availability of high surface area to the reactants to react on the surface of catalyst.

The energy dispersive X-ray spectrum (EDS) was recorded by using an INCA x-act Oxford instrument (Model 51-ADD0007). The EDS analysis shows the elements present in the material. EDS analysis of fresh $Pd(OAc)_2Ph_2PEt@SiO_2$ catalyst shows the presence of Si, P, O, Pd elements (Fig. 2).

2.3. General experimental procedure for synthesis of alkenes via semi-hydrogenation of alkynes

To a 100 mL high-pressure reactor, phenylacetylene (1 mmol), Pd (0.96 mol%) in a 10 mL THF were transferred under an inert atmosphere. The reactor was flushed three times with nitrogen

Table 3
Effect of catalyst loading study for low conversion (ideally around 20%).

Entry	Catalyst in mg (mol%)	Conversion of **1a** (%)[a]	Selectivity **2a/3a** (%)[b]
1	10 (0.6 mol%)	95	95/5
2	8 (0.48 mol%)	89	92/8
3	6 (0.36 mol%)	80	91/9
4	4 (0.24 mol%)	70	93/7
5	2 (0.12 mol%)	60	95/5
6[c]	2 (0.12 mol%)	19	94/6

[a] Reaction Conditions: 1a (1 mmol), syngas (150 psi), THF (10 mL), temp. (70 °C), time 6 h.
[b] GC Yield.
[c] time 2 h.

Table 4
Effect of temperature study for low conversion (ideally around 20%).

Entry	Temperature (°C)	Conversion of **1a** (%)[a]	Selectivity **2a/3a** (%)[b]
1	70	97	98/2
2	60	92	95/5
3	50	23	94/6
4	40	21	93/7
5	30	NR	–
6[c]	30	NR	–
7[d]	30	NR	–

[a] Reaction Conditions: 1a (1 mmol), catalyst (15 mg), syngas (150 psi), THF (10 mL), time (6 h).
[b] GC Yield.
[c] Reaction time 4 h.
[d] Reaction time 2 h.

then pressurized with desired 150 psi of syngas, then heated at 70 °C with constant stirring (400 rpm) for 6 h. After the completion of reaction, the reactor cooled down to room temperature and the remaining syngas was carefully depressurized. The resultant reaction mixture filtered off by simple filtration. The filtrate was then collected in sample vial and the product was extracted for further analysis such as GC, GC–MS, ^1H & ^{13}C NMR and matched with those of authentic data. Selective experiments were performed in triplicate and it was observed that results showed variation of ±2%.

2.4. General experimental procedure for recycling of $Pd(OAc)_2Ph_2PEt@SiO_2$ catalyst

After the completion of reaction, the reaction mixture was cooled to room temperature and the catalyst was recovered by simple filtration. The filtered catalyst was washed with methanol (3 × 5 mL) to remove all traces of product or reactant present. The filtered catalyst was then dried under reduced pressure for 5 h. The dried catalyst was then used for the next run for the recyclability experiment of semi-hydrogenation of alkynes.

3. Results and discussion

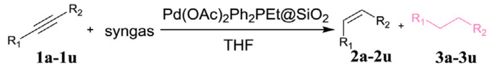
Initially, our aim was to develop a heterogeneous catalytic system for the hydroformylation of terminal alkynes to the synthesis of α,β-unsaturated aldehydes. Under the hydroformylation reaction conditions phenylacetylene provided an unexpected results by using as prepared $Pd(OAc)_2Ph_2PEt@SiO_2$ catalyst i.e., instead of hydroformylation the semi-hydrogenated styrene obtained as major product with trace amount of complete hydrogenation product. This unexpected result inspired us to focus on the selective semi-hydrogenation of alkynes for the synthesis of alkenes. The semi-hydrogenation of phenylacetylene to styrene was chosen as model reaction for optimization study. The various reaction parameters such as catalyst screening, loading, the effect of syngas (CO/H_2) pressure, time, temperature and solvents were studied for the selective semi-hydrogenation of phenylacetylene (**1a)** and the results are summarized in Tables 1 and 2. Firstly, we screened various homogeneous and heterogeneous Pd catalysts (Table 1, entries 1–5). It was observed that $Pd(OAc)_2Ph_2PEt@SiO_2$ provided high conversion of **1a** with excellent selectivity toward the formation of styrene (**2a**) (Table 1, entry 3). The Pd/C (10%) catalyst provides good conversion for semi-hydrogenation reaction of **1a** but selectivity of **2a** was less than prepared $Pd(OAc)_2Ph_2PEt@SiO_2$ catalyst (Table 1, entry 4). With increase in the catalyst loading, a significant increase in conversion, but selectivity of **2a** drastically decreases (Table 1, entries 8, 9 and 10). The formation of products (**2a** and **3a**) was not observed in absence of the catalyst (Table 1, entry 11) it indicates that catalyst is solely responsible for the reaction.

Furthermore, in order to increase the conversion of **1a** and selectivity of **2a**, we investigated the effect of syngas (CO/H_2) pressure on the model reaction at 80 °C for 10 h in THF as solvent. At 300 psi of syngas pressure reaction provides conversion (82%) and selectivity (89%) of desired product **2a** (Table 2, entry 1). It was observed that, decrease in the syngas pressure at 200 psi, the conversion (85%) and selectivity (95%) of **2a** increases (Table 2 entry 2). It was noted that both the conversion as well as selectivity was better at 150 psi pressure of syngas (Table 2, entry 3). The decrease in syngas pressure below 150 psi the conversion of starting material and selectivity was less (Table 2, entry 4).

Moreover, we studied the effect of relative stoichiometric ratio of carbon monoxide (CO) and hydrogen (H_2) gas (Table 2, entries 5–8). As the relative concentration of CO with respect to H_2 increases, the conversion of **1a** and selectivity of corresponding product **2a** decreases (Table 2, entry 5). On the other hand, with increase in the concentration of H_2 with respect to CO, the conversion of **1a** increases but considerably decreases the selectivity toward **2a** (Table 2, entry 6). Therefore, we kept equal ratio (1:1) of CO and H_2 gas as it provides the high conversion of **1a** with excellent selectivity toward **2a** (Table 2, entry 3). These results clearly indicate that the syngas (CO/H_2) favors this transformation. No reaction occurs only in presence of CO atmosphere (Table 2, entry 7). At 150 psi pressure of H_2 gas, 100% conversion of **1a** takes place but instead of **2a** complete hydrogenation product **3a** was observed (Table 2, entry 8).

Next, we investigated that the effect of time, temperature and solvent for the effective progress of the reaction. The optimum reaction time could be reduced to 6 h (Table 2, entry 10). Decreasing the reaction temperature beyond 6 h lead to a significant decrease in the conversion and selectivity of product **2a** (Table 2, entry 11). Further, we checked the effect of temperature on the reaction and it was found that the conversion of **1a** increases with increase in the reaction temperature from 60 °C to 90 °C, but a gradual decrease in the selectivity of **2a** was also noted (Table 2, entries 3 and 12–14). Increasing the reaction temperature beyond 90 °C did not show any significant effect on the conversion, but drastically decreases the selectivity of **2a** (Table 2, entry 15). The temperature of 70 °C was the optimized reaction temperature for the reaction to get the excellent selectivity of product **2a** (Table 2, entry 13). Moreover, the effects of different solvents were investigated for the reaction. Various polar and non polar solvents such as THF, 1,4-dioxane,

Table 5
Substrate study for semi-hydrogenation of alkynes[a].



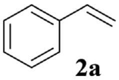
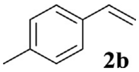
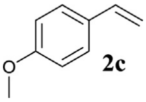
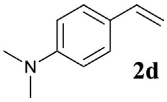
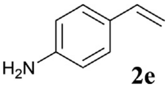
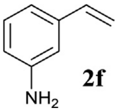
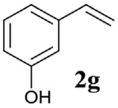
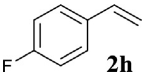
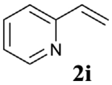
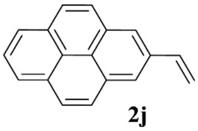
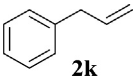
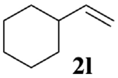
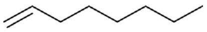
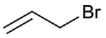
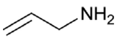
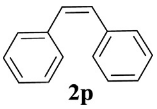
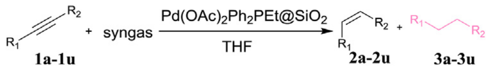
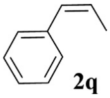
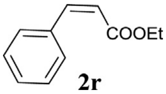
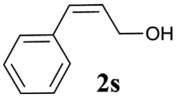
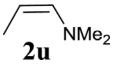
Entry	Products **2a–2u**	Conversion of **1a–1u** (%)[a]	Selectivity **2a–2u/3a–3u** (%)[b]
Terminal alkynes			
1	 **2a**	97	98/2
2	 **2b**	94	96/4
3	 **2c**	92	97/3
4	 **2d**	93	94/6
5	 **2e**	94	92/8
6	 **2f**	90	92/8
7	 **2g**	92	94/6
8	 **2h**	90	92/8
9	 **2i**	85	94/6
10	 **2j**	89	85/15
11	 **2k**	97	98/2
12	 **2l**	95	98/2
13	 **2m**	84	91/9
14	 **2n**	82	90/10
15	 **2o**	85	92/8
Internal alkynes			
16[c]	 **2p**	60	98/2

Table 5 (*Continued*)



Entry	Products **2a–2u**	Conversion of **1a–1u** (%)[a]	Selectivity **2a–2u/3a–3u** (%)[b]
17	 **2q**	89	96/4
18	 **2r**	92	87/13
19	 **2s**	94	96/4
20	 **2t**	92	95/5
21	 **2u**	90	95/5

[a] Reaction Conditions: alkyne (1 mmol), THF (10 mL), Pd catalyst (0.96 mol%), 400 rpm, CO/H_2 (150 psi), Time (6 h).
[b] GC Yield.
[c] Time (12 h), Temp. (100 °C).

ethanol, methanol, toluene and DMF were screened (Table 2, entries 3, 16–20). Among them, THF was found to be a best solvent which provided high conversion and an excellent selectivity toward **2a** (Table 2, entry 13).

We studied the effect of catalyst loading for low conversion (ideally around 20%), the loading of 0.6 mol% $Pd(OAc)_2Ph_2PEt@SiO_2$ catalyst provides high conversion up to 95% (Table 3, entry 1). We decrease the catalyst loading gradually from 0.6 mol% to 0.12 mol% to check the reaction performance for low conversion (Table 3, entries 1–6), the catalyst loading of 0.12 mol% provides low conversion of 19% at 2 h (Table 3, entry 6).

We also studied the effect of reaction temperature for the little conversion about 20%. The temperature of 70 °C and 60 °C affords high conversion of **1a** about 97% and 92% respectively (Table 4, entry 1 and 2). But a sudden change from high to low conversions of **1a** was observed 23% and 21% when temperature decreased at 50 °C and 40 °C respectively (Table 4, entries 3 and 4).

These optimized reaction conditions were further applied to investigate the wide substrate applicability of this protocol. Phenylacetylene bearing electron-donating group such as —Me, —OMe, —NMe_2, —NH_2, —OH (**2b–2 g**) and electron withdrawing group —F (**2 h**) resulted into an excellent selectivity toward corresponding alkenes (Table 5, entries 2–8). The alkyne containing heteroatom (**1i**) could also be reduced successfully providing 94% selectively of the desire product **2i** (Table 5, entry 9). The terminal alkynes (**2j–2o**) were easily reduced to corresponding products with 85–98% selectivity (Table 5, entries 10–15). To our delight, aromatic and aliphatic internal alkynes can be smoothly converted in to the respective alkenes providing 87–98% selectivity. The alkyne **1p** provided moderate conversion but selectivity of **2p** is excellent at high temperature (100 °C) for longer reaction time of 12 h (Table 5, entry 16). The various aromatic and aliphatic internal alkynes (**1q–1u**) were reduced to corresponding alkenes providing moderate to high conversion as well as selectivity (Table 5, entry 17–21).

4. Catalyst reusability

The recyclability study of Pd-catalyst was examined for the synthesis of styrene by semi-hydrogenation of **1a** with synthesis under the optimized reaction conditions. After completion of reaction, the reactor was cooled to room temperature and remaining syngas vented out carefully. The catalyst was recovered by simple filtration and then washed three times with THF and finally by methanol to remove traces of organic contents. The resulting catalyst was dried under vacuum for 5 h and could be recycled up to four consecutive cycles (Fig. 3). In order to prove that there was no catalyst leaching, the mother liquor were examined for each run by ICP-AES technique. The results indicates that the palladium in the mother liquor were below to the detectable level.

The XPS analysis was performed for the fresh, first and fourth recycled catalyst as shown in Fig. 4. The wide scan of the fresh and recycled $Pd(OAc)_2Ph_2PEt@SiO_2$ catalyst [Fig. 4(a)] which indicates the presence of P, C, Pd, O, and Si elements in the catalyst. The XPS spectra of $Pd(OAc)_2Ph_2PEt@SiO_2$ catalyst shows that two peaks at 334.6 and 340.5 eV for fresh $Pd(OAc)_2Ph_2PEt@SiO_2$ are assigned as $3d_{5/2}$ and $3d_{3/2}$ for Pd^{2+} species, respectively [Fig. 4(b)]. For the first recycle sample, no change in peaks appear at 334.5 and 340.5 eV, which are assigned as $3d_{5/2}$ and $3d_{3/2}$ for Pd^{2+} species, respectively, indicating that the no change in oxidation state of Pd during the catalytic reaction. From the spectrum of the fourth recycle sample, it is obvious that the component of Pd^{2+} is slightly decreasing upon recycles, although the component of Pd^{2+} remains constant. The peak at 129.8 eV corresponds to the P2p recognized to the presence of phosphine in the catalyst shown in Fig. 4(c). The peak at 192.5 eV corresponds to the P2s recognized to the presence of phosphine in the catalyst shown in Fig. 4(d). These results indicate that the coordination bond between Pd and phosphine are formed and they are still remains on silica support even after 4th recycle.

The SEM images of fresh, 1st recycled and 4th recycled $Pd(OAc)_2Ph_2PEt@SiO_2$ catalysts are shown in (Fig. 5), which shows the surface morphology of the catalyst. The FEG-SEM analy-

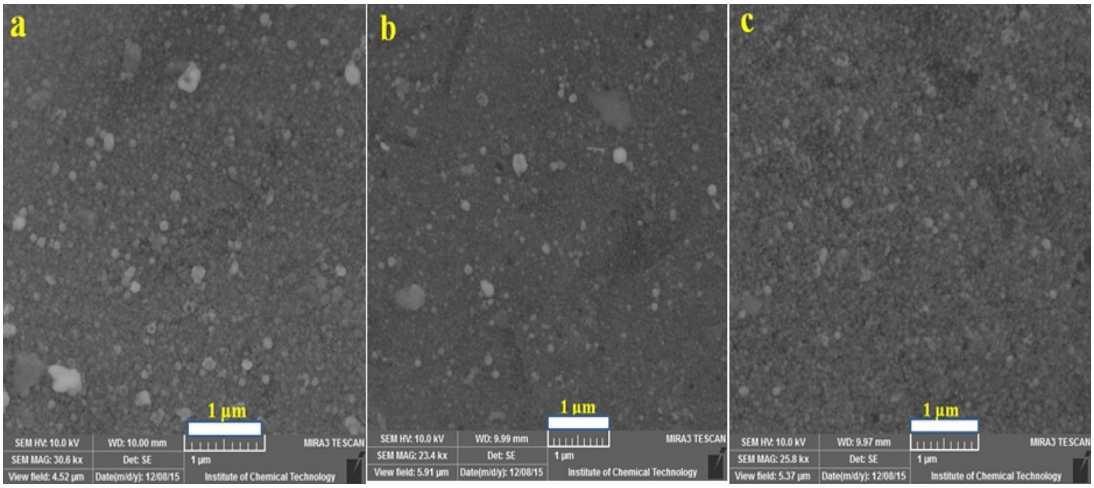


Fig. 5. FEG-SEM images of (a) fresh, (b) 1st recycled and (c) 4th recycled $Pd(OAc)_2PPh_2Et@SiO_2$ catalyst.

sis of fresh and recycled catalyst points the Pd species present on the surface of catalyst. After the 4th recycled the palladium metal slightly agglomerized on the surface of the catalyst [Fig. 5(c)]. The SEM images of fresh, 1st recycled and 4th recycled $Pd(OAc)_2Ph_2PEt@SiO_2$ catalysts with metal mapping acquired using EDX analysis are shown in Fig. S2, 4 and 6 respectively (please see in the supporting information). It shows that the Pd species is well dispersed on the surface of catalyst.

5. Conclusions

In conclusion, we have developed a simple, efficient, heterogeneous $Pd(OAc)_2Ph_2PEt@SiO_2$ catalyst and used for the synthesis of alkenes *via* semi hydrogenation reaction of alkynes using syngas as a hydrogen source. In the present protocol, the syngas contains an equal ratio of carbon monoxide and hydrogen gas is used as a controlling system to prevent the rate of over hydrogenation. The present catalytic system eliminates the use of poisonous metals, additives, co-catalysts and excess amount of chemicals. This developed method tolerates wide range of internal as well as terminal alkynes and affords the respective alkenes from moderate to high conversion (60–97%) with good to excellent selectivity (85–98%). The catalyst could be easily recovered and shows significant recyclability up to the fourth run without loss of its catalytic activity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2016.01.004.

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