



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/H₂). 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 Emission Gun Scanning Electron Microscopy (FEG-SEM), Energy Dispersive X-ray Spectroscopy (EDS), X-ray Photoelectron Spectroscopy (XPS), Inductively Coupled Plasma- Atomic Emission 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.

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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

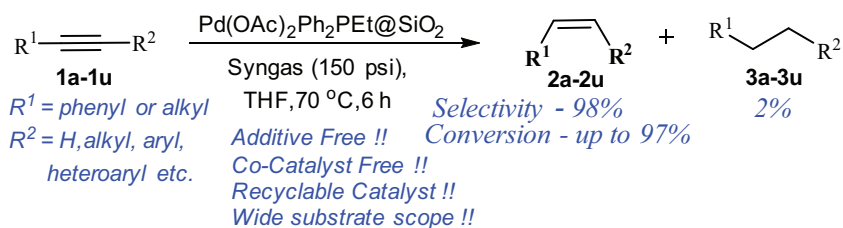
[19], Rh [20,21], Ir [22] and Ru [23]. Despite the potential utility of Lindlar catalyst (Pd/CaCO₃) treated with Pb(OAc)₂) suffers from drawbacks such as use of poisonous lead (Pb) salt and excess use of quinoline to control the over hydrogenation, which limits in the substrate scope and selectivity [24]. Heterogeneous catalysis based on Pd and Ni metals has been extensively studied for reduction of alkynes to Z-alkenes using H₂ 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/NEt₃. In this method, HCOOH served as a hydrogen source and NEt₃ 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.

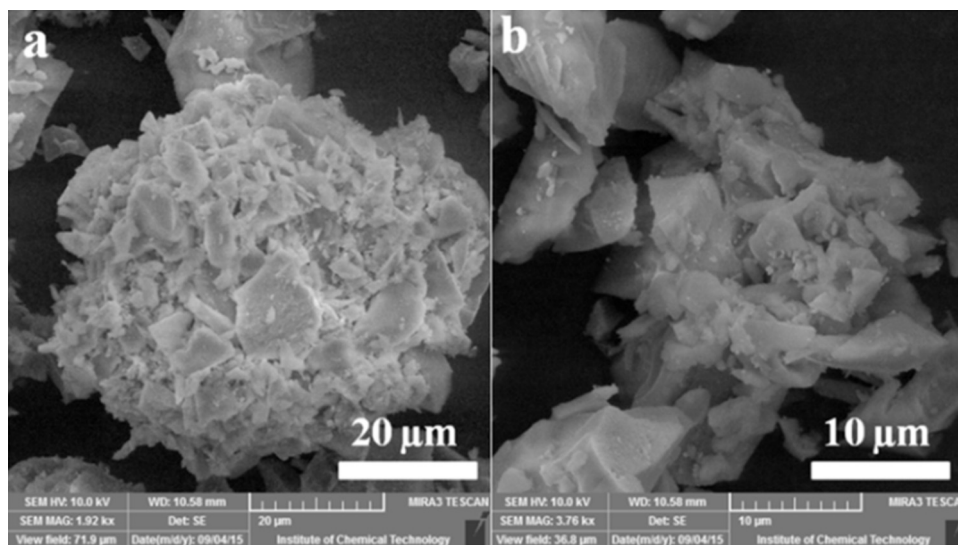


Fig. 1. FEG-SEM images of Pd(OAc)₂Ph₂PEt@SiO₂ fresh catalyst before the reaction.

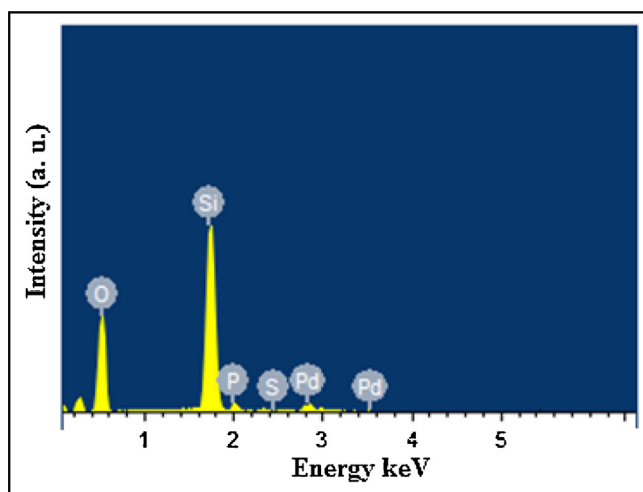


Fig. 2. EDS image of fresh Pd(OAc)₂Ph₂PEt@SiO₂ catalyst.

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 from Sigma Aldrich, S.D. Fine and commercial suppliers. The solvents were purchased from commercial suppliers and used without further purification. The prepared Pd(OAc)₂PPh₂Et@SiO₂ 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)₂PPh₂Et@SiO₂ 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 × 5 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 CDCl₃ solvent (¹H, 400 MHz; ¹³C, 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-

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