

## Research Article

# Rapid Reduction of Alkenes and Alkynes over Pd Nanoparticles Supported on Sulfonated Porous Carbon

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A novel method has been introduced for rapid reduction of alkenes and alkynes, which may be attractive for chemical industries. This method has some advantages such as simplicity and low cost of reactants. Pd supported on sulfonated porous carbon (SPC) was used as a new catalyst for reduction of alkenes and alkynes to the corresponding alkanes using sodium borohydride. The heterogeneous reaction was conducted in open air at room temperature to produce the desired saturated compounds in high yields (over 96%) and in short reaction time (15 minutes).

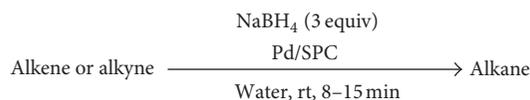
## 1. Introduction

Catalytic hydrogenation is one of the most widely used methods for addition of hydrogen to unsaturated hydrocarbons. Unsaturated hydrocarbons including alkenes and alkynes can be reduced to corresponding saturated alkanes with the use of common transition metal catalysts, particularly, platinum, palladium, rhodium, ruthenium, and nickel. Finely dispersed metal powders, or adsorbed metal powders on inert supports such as carbon or alumina, and certain soluble complexes of these metals also exhibit good catalytic activity for this kind of catalytic hydrogenation [1, 2]. Since these methods require performing the catalytic reductions at high temperatures ( $>50^{\circ}\text{C}$ ) and high pressures of  $\text{H}_2$  gas ( $>5$  bar) as well as using an external source of molecular hydrogen, they have some shortcomings for their applications and safety [3].

Brown and coworkers have introduced a suitable method for synthesis of sodium borohydride ( $\text{NaBH}_4$ ) as a suitable source of hydrogen gas, which can be used for hydrogenation [4, 5]. This reagent has opened new insights for the reduction of functional groups in organic synthesis. Since  $\text{NaBH}_4$  is being the least expensive and commercially available metal hydride, safe to use and storage, capability to use in different solvents, reducing different functional groups with chemo-, regio- and diastereoselectivities, and easy work-up procedure, it is a valuable metal hydride [6–12]. Sodium

borohydride with various simple metal salts can also be used for selective reduction of some classes of organic compounds [13–22]. Moreover, a diversity of hydride reagents combined with both simple and complex salts of palladium, rhodium, nickel, indium, and the other metals have developed to perform selective hydrogenation of alkenes and alkynes [23–29]. For organic chemists and chemical industries, it is useful to extend the application of sodium borohydride for reduction of any unsaturated alkenes and alkynes with a cheap method.

Due to environmental and economic considerations in recent years, heterogeneous catalysts have been gained some advantages with respect to the homogeneous systems, for example, ease of recovery, recycling, and enhanced stability. Porous carbon materials are attractive because of their huge laboratory and industrial applications for production of complex organic compounds [30–32]. They can be used as supports for different catalytic processes, fuel cells, and capacitors. They may also contain high surface areas and well-developed porosities, which are used widely during recent years because they can fulfill most of the desirable properties required for a suitable catalyst support. They have several advantages, including the stability in aggressive media at elevated temperature, feasibility of control parameters of the porous structure surface area in a broad range, and the physicochemical properties [33–46].



SCHEME 1

The purpose of this work is to prepare Pd supported on sulfonated porous carbon (SPC) for reduction of alkenes and alkynes to saturated alkanes by sodium borohydride. In this work, a modification of Brown's work was applied, which include the direct use of Pd supported on SPC as heterogeneous catalysts instead of a mixture of metal salts or palladium metal and acid reagent [47]. It is shown that the new catalyst performed the reduction reactions very cleanly, and the reaction times are also clearly improved. Moreover, the presented method can be used for those unsaturated substrates having high resistance to reduce through Brown's original method (Scheme 1).

## 2. Experimental

**2.1. General Experimental Information.** Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. All reactions were monitored by GC, and all yields refer to isolated products.  $^1\text{H-NMR}$  spectra were recorded on a Bruker-Avance AQS 300 MHz using tetramethylsilane (TMS) as an internal standard. Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet IMPACT 400D instrument. X-ray diffraction patterns (XRD) were obtained on a Bruker D8 ADVANCE instrument. The specific surface area and mean pore diameter ( $d_p$ ) were calculated from adsorption isotherms of nitrogen at 77 K using the standard Brunauer-Emmett-Teller (BET) equation and were obtained on a NOVA 2200, Quantachrome Corporation, version. Scanning electron microscopy images (SEM) were taken on SEM Philips XL30. Transmission electron microscope (TEM) images were obtained using an LEO-960E at a voltage of 80 kV. GC-Mass analysis was carried out using Fisons TRO 1000 spectrometer.

**2.2. Preparation of SPC.** Pine wood powder was used as starting material in the preparation of porous carbon (PC) material. In a typical procedure, wood powder (10 g) was impregnated with  $\text{ZnCl}_2$  by immersion in aqueous solution of HCl (1.0 M, 50 mL) containing  $\text{ZnCl}_2$  (20 g) under mechanical agitation at 25°C for 15 h. After that, the supernatant liquid was separated by filtration, and the remaining solid was oven-dried at 80°C for 24 h. Then, the  $\text{ZnCl}_2$ -impregnated wood powder was placed in a boat-like small size ceramic container and heated gradually from room temperature to 500°C. The heating gradient was not faster than 10°C  $\text{min}^{-1}$ . The heating time at maximum heat (500°C) treatment temperature was 1 h. Thereafter, the sample was washed by heating in the aqueous HCl solution (5%, 100 mL) at 100°C for 1 h. Then, the resulting solid was filtered and rinsed with warm distilled water (50°C) to confirm that the wash solution is free of zinc ions. The resultant activated

porous carbon material was finally dried at 80°C in an oven for approximately 24 h. Then, the activated porous carbon material (5 g) was heated for 15 h in oleum (18–24 wt%  $\text{SO}_3$ , 100 mL) at 180°C under  $\text{N}_2$  in order to introduce  $\text{SO}_3\text{H}$ . After heating and then cooling to room temperature, distilled water (400 mL) was added to the mixture. The black precipitate was filtered and repeatedly washed with boiling distilled water until impurities such as sulfate ions were no longer detected in the wash water. The sample was finally dried overnight in an oven at 80°C to afford the sulfonated acid catalyst [44–46, 48].

**2.3. Preparation of Pd/SPC.** Nanoparticles of Pd loaded on sulfonated porous carbon were synthesized at room temperature by chemical reduction using  $\text{NaBH}_4$  as follows: carbon material (0.2 g) was added to aqueous  $\text{PdCl}_2\text{-HCl}$  solution (2.86 mmol/L, corresponding to 1.5 wt% of Pd, 10 mL), and the mixture was stirred for 30 min. Excess amounts of  $\text{NaBH}_4$  solution (0.02 M) were added, and the mixture was further stirred for 3 h. The resulting suspension was filtered, washed with distilled water several times, and dried at 80°C overnight [49, 50].

**2.4. Typical Procedure.** A mixture of Pd/SPC,  $\text{NaBH}_4$  (12 mmol), and alkene or alkyne (4 mmol) was pulverized in a mortar for 1 min. Then, the mixture was introduced into a 25 mL flat-bottomed flask, and water (12 mL) was added slowly to it. The reaction mixture was magnetically stirred continuously at room temperature for specific time periods. Thereafter, dilute HCl solution (5%) was added dropwise to quench the reaction until gas evolution ceased and extracted with *n*-pentane or ether ( $3 \times 10$  mL). The organic portions were combined, dried over  $\text{MgSO}_4$ , and filtered. After that, the pure corresponding alkane was obtained by removal of the solvent under reduced pressure. Reactions were typically analyzed and authenticated by GC-MS and/or  $^1\text{H-NMR}$  technique.

## 3. Results and Discussion

The X-ray diffraction patterns of the SPC and Pd/SPC are shown in Figure 1. The XRD pattern of SPC (Figure 1(a)) exhibits one broad and weak diffraction peak ( $2\theta = 10\text{--}30^\circ$ ) attributed to the amorphous carbon. In the sample, 1.5% Pd/SPC (Figure 1(b)) peaks attributed to the metallic palladium were observed. The XRD pattern exhibited three peaks at  $2\theta$  of 40°, 46°, and 68°, ascribed, respectively, to (111), (200), and (220) reflections of Pd metal with a face-centered cubic (fcc) structure [49, 51].

The FT IR spectrum of Pd/SPC (Figure 2) shows a broad band at 3300–3500  $\text{cm}^{-1}$ , which is assigned to OH groups.

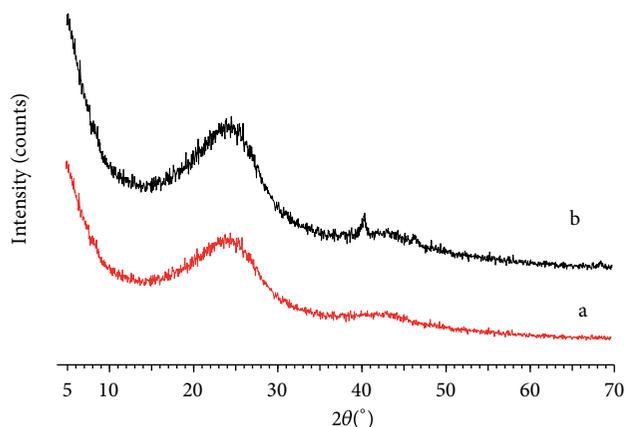


FIGURE 1: The X-ray diffraction patterns of the SPC (a) and Pd/SPC (b).

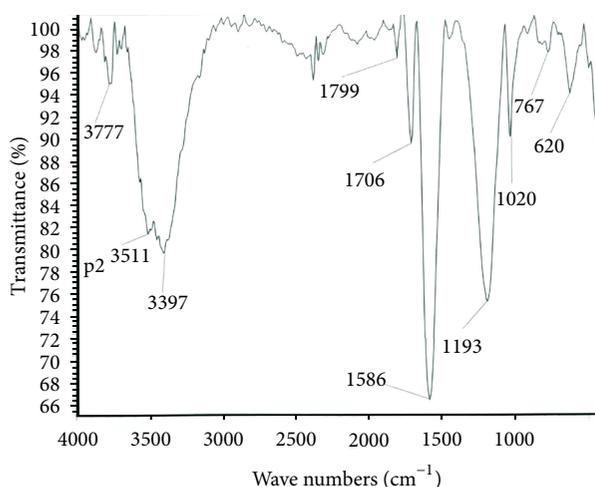


FIGURE 2: The FT-IR spectrum of the Pd/SPC.

The vibration bands at 1020 and 1193  $\text{cm}^{-1}$  in spectrum indicate that the resulting material possesses  $\text{SO}_3\text{H}$  groups [52, 53].

The morphologies of Pd/SPC composite materials have been investigated by TEM (Figure 3) and SEM (Figure 4). It can be seen that Pd nanoparticles are well dispersed on the surface of Pd/SPC composite materials with a diameter under 40 nm. SEM of the sample after the deposition of Pd on the carbon support (Figure 4) shows that the palladium particles dispersed on the support.

The BET surface area of Pd/SPC was calculated from the adsorption isotherm of nitrogen at 77 K. The surface area was 910  $\text{m}^2 \text{g}^{-1}$ .

The density of  $\text{SO}_3\text{H}$  group of Pd/SPC was determined on the basis of elemental analysis. Total acid densities ( $\text{SO}_3\text{H} + \text{COOH}$ ) and ( $\text{SO}_3\text{H} + \text{COOH} + \text{OH}$ ) were obtained using standard acid-base back titration with two bases of different strength, that is,  $\text{NaHCO}_3$  and  $\text{NaOH}$  solutions. The results

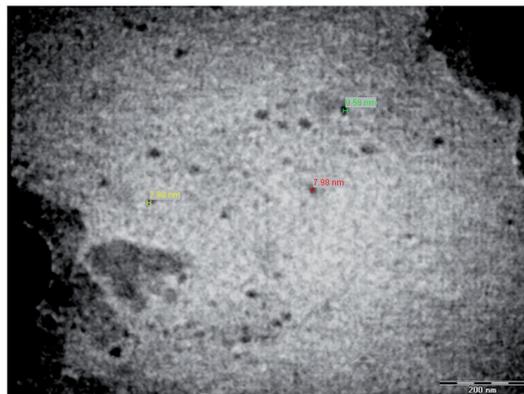


FIGURE 3: TEM image of Pd/SPC composite materials.

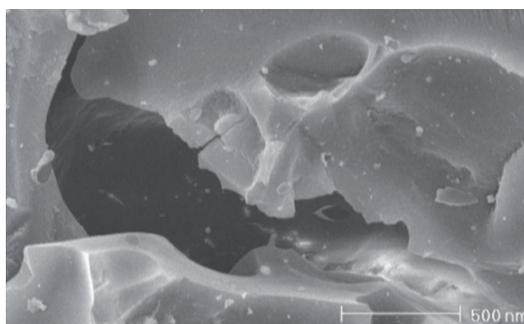


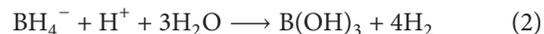
FIGURE 4: SEM image of Pd/SPC composite materials.

revealed that the amounts of  $\text{SO}_3\text{H}$ ,  $\text{COOH}$ , and phenolic  $\text{OH}$  groups are 3.41, 0.13, and 1.01  $\text{mmol g}^{-1}$ , respectively.

The amount of produced hydrogen gas from  $\text{NaBH}_4$  is calculated on the basis of the following reaction:



One mole of  $\text{NaBH}_4$  reacts with two moles of water that produces four moles of hydrogen gas. Due to pH stabilization of the reaction medium, the reaction of  $\text{NaBH}_4$  with water results in a low hydrogen gas yield. This pH stabilization is caused by formation of the strongly basic metaborate ions [54, 55]. The addition of acids delays the formation of the metaborate ions by shifting the pH of the reaction medium to lower values, which allows improved hydrogen gas yield. In acidic solutions, the hydrolysis of  $\text{NaBH}_4$  proceeds as follows:



The percentage yield of hydrogen gas obtained from the reaction of  $\text{NaBH}_4$  with water and SPC, various concentrations of Pd/SPC, and PC are compared in Table 1. Several observations can be drawn from a comparative study of these results. For instance, it is evident that Pd/SPC and SPC facilitate an increase in the hydrogen gas yield. The hydrogen gas yield is significantly lower with the addition of Pd/PC as shown in Table 1 as compared to Pd/SPC.

The overall hydrogenation process is viewed in a series of reversible and sequential steps, as summarized in Figure 5.

TABLE 1: Hydrogen yield from the hydrolysis of NaBH<sub>4</sub> in different concentrations at 25°C.

Entry	NaBH <sub>4</sub> (g)	Activator (g) (Pd/SPC)	Ratios H <sup>+</sup> /NaBH <sub>4</sub>	Water (mL)	Hydrogen yield (%)	Time (min)
1	0.151 (4 mmol)	—	—	4	27.5	60
2	0.151 (4 mmol)	0.44 (2.0 mmol H <sup>+</sup> )	0.5	4	73	2
3	0.151 (4 mmol)	0.88 (4 mmol H <sup>+</sup> )	1.0	4	94	2
4	0.151 (4 mmol)	1.76 (8 mmol H <sup>+</sup> )	2.0	4	99.7	2
5	0.151 (4 mmol)	2.64 (12 mmol H <sup>+</sup> )	3.0	4	100	1
6	0.151 (4 mmol)	1.75 (8 mmol H <sup>+</sup> )	2.0	2	99.0	2
7	0.151 (4 mmol)	1.76 (8 mmol H <sup>+</sup> )	2.0	1	97	2
8	0.151 (4 mmol)	1.76 (8 mmol H <sup>+</sup> )	2.0	0.5	87	3
9	0.151 (4 mmol)	1.76 (8 mmol H <sup>+</sup> )	2.5	—	5	120
10	0.151 (4 mmol)	SPC <sup>a</sup> 1.70 (8 mmol)	2.0	4	96.3	2
11	0.151 (4 mmol)	Pd/PC <sup>b</sup> (1.41)	—	4	56.2	60

<sup>a</sup>SPC: sulfonated porous carbon (CH<sub>0.45</sub>O<sub>0.38</sub>S<sub>0.074</sub>).

<sup>b</sup>PC: porous carbon (CH<sub>0.47</sub>O<sub>0.09</sub>).

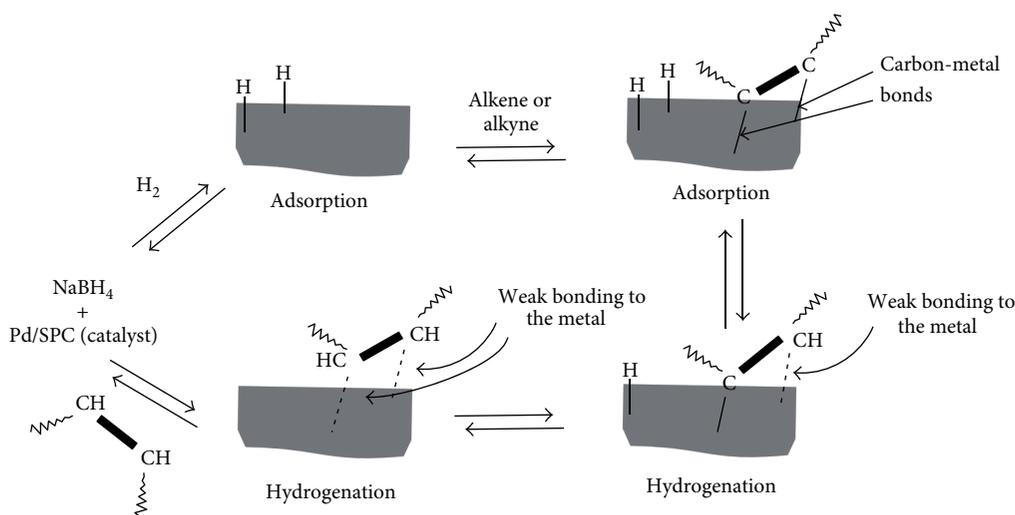


FIGURE 5: A possible mechanism for catalytic hydrogenation.

First, the reactants including hydrogen and alkenes or alkynes are adsorbed on the surface of the metal catalyst. The energies of the metal-hydrogen and metal-carbon bonds are such that, in a second step, an atomic hydrogen gas is transferred to carbon to give an alkyl attached to Pd. This is the halfway point on hydrogenation. In the next step, the Pd-carbon bond is broken, and the second carbon-hydrogen bond is formed. Hydrogenation is now complete, and the product is desorbed from the catalyst surface. The produced corresponding alkane molecule has a low affinity for the metal surface and, when desorbed, creates a vacant space for the adsorption of new alkenes or alkynes and hydrogen molecules [56–61].

These results prompted us to investigate the optimum reaction conditions for reduction of alkenes and alkynes in presence of Pd/SPC. In optimized procedure, the ratio of Pd/SPC (H<sup>+</sup>)-NaBH<sub>4</sub> is lesser than 1.0. For higher ratios of Pd/SPC-NaBH<sub>4</sub>, the rate of hydrolysis of NaBH<sub>4</sub> increases,

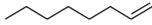
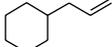
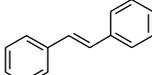
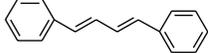
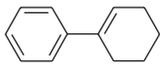
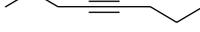
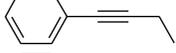
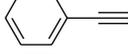
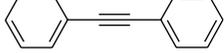
whose results exit of bubbles of hydrogen gas from reaction media.

Depending on the substrate, reduction is rapid and largely complete in as little as 15 min. The products of alkanes are obtained in fairly pure form by workup, extraction with pentane or ether, drying, and evaporation of the solvent under reduced pressure. For different substrates where we examined, all of the reductions were completed up to 96% with less than 15 min.

The procedure is extremely convenient for which the reduction takes place at room temperature in open air. The amount of used palladium (1.5% wt) was based on achieving reaction time less than 15 min. Typical results are given in Table 2.

To check the reusability and recyclability of the catalyst (Pd/SPC), we have carried out the reduction of styrene under similar reaction conditions. The catalyst was separated by

TABLE 2: Reduction of alkynes and alkenes to the corresponding alkanes at room temperature.

Substrate	Catalyst loadings (mol% Pd/SPC)	Time (min)	Conversion <sup>a</sup> (%)
	3	10	99 (89) <sup>b</sup>
	3	10	99 (91) <sup>b</sup>
	3	10	99 (95) <sup>b</sup>
	3	8	98(95) <sup>b</sup>
	3	10	99 (95) <sup>b</sup>
	3	10	98 (83) <sup>b</sup>
	5	15	99 (96) <sup>b</sup>
	5	10	98(95)
	3	10	99 (90) <sup>b</sup>
	3	10	99 (90) <sup>b</sup>
	5	15	96 (82) <sup>b</sup>
	5	15	98 (90) <sup>b</sup>
	5	15	98 (84) <sup>b</sup>
	5	10	99 (90) <sup>b</sup>
	5	15	99 (87) <sup>b</sup>

<sup>a</sup>Determined by GC/MS analysis. <sup>b</sup>Isolated yields.

filtration after completion of the reaction. It has also been dried and used for subsequent experiments after adding fresh substrate and NaBH<sub>4</sub> under similar reaction conditions. For three catalytic cycles, the yields and reaction times remained the same. The reaction time was found to increase gradually with comparable yields of the ethylbenzene in subsequent recycle experiments.

#### 4. Conclusions

We have developed an aqueous and general efficient method for the environmentally safe reduction of alkynes and alkenes using sulfonated porous carbon supported by nano-Pd as a new heterogeneous catalyst system in the presence of NaBH<sub>4</sub>. The results have shown that palladium nanoparticles immobilized in a well-dispersed way on the outer surface of that sulfonated porous carbon.

The usefulness and versatility of the presented method was confirmed with the reduction of several alkenes and alkynes to corresponding alkanes without an external source of hydrogen gas in short reaction times and excellent yields.

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