Selective transfer hydrogenation of phenol to cyclohexanone on supported palladium catalyst using potassium formate as hydrogen source under open atmosphere

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ARTICLE INFO

Article history:
Received 7 February 2015
Received in revised form 27 March 2015
Accepted 8 April 2015
Available online 20 April 2015

Keywords:
Transfer hydrogenation
Heterogeneous catalysis
Cyclohexanone
Phenol
Open atmosphere

ABSTRACT

A selective, effective and sustainable catalytic transfer hydrogenation of phenol to cyclohexanone on supported palladium using potassium formate as benign hydrogen source at atmospheric pressure and mild reaction conditions has been demonstrated. A reaction temperature, catalyst (Pd/C), solvent (water) quantity and type of hydrogen source are found to be most influencing factors for effective phenol conversion. Hydrogen donor potassium formate playing important dual role; as hydrogen source and as additive to enhance the cyclohexanone selectivity. The catalyst Pd/C has successfully recovered through filtration and reused up to few batches without considerable loss of phenol conversion and cyclohexanone selectivity.

1. Introduction

Hydrogenation of phenol to cyclohexanone has been subject of continuous interest and it is widely studied [1]. Cyclohexanone is known as one of the key chemicals in the synthesis of caprolactam and adipic acid, which are the main ingredients for the preparation of Nylon 6, Nylon 66 and polyamide resin [2].

Traditionally, phenol hydrogenation has been carried out in gas phase, with supported Pd or Pt catalysts as efficient systems for this reaction [3–6]. However, high temperatures are normally required for this process (150–300 °C), and the generation of carbonaceous deposits (CO) in the course of the reaction leads to deactivation of the catalyst [7]. The effect of various reaction parameters (solvents, temperature, support nature) in the phenol hydrogenation on palladium/carbon (Pd/C) has been studied in the literature [8–10]. More recently, mild (below or at 100 °C temperature) liquid-phase phenol hydrogenation protocols have been continuously studied under variable molecular hydrogen pressure using heterogeneous supported palladium catalysts [11,12]. The selective phenol hydrogenation to cyclohexanone using palladium catalysts was also reported [13,14]. However, hydrogen (H₂) is potentially dangerous, expensive and has some limitations such as necessity of special facilities for H₂ generation, storage, and transportation [1].

Alternative to molecular H₂: in situ hydrogen generated through aqueous phase reforming (APR) of methanol on supported palladium catalysts (Pd/Al₂O₃, Pd-La₂O₃/Al₂O₃) has been utilized for the hydrogenation of phenol [15,16]. Formic acid (HCOOH) is another in situ hydrogen source reported for catalytic phenol hydrogenation using Pd/C [17]. Sodium formate (HCOONa) has been also utilized as in situ hydrogen source for the catalytic phenol hydrogenation using Pd/C [18], Pd-PANI/CNF [19] and RuCl₂/PPH₃ [20]. However these phenol hydrogenation protocols (using methanol or ethanol, formic acid and sodium formate) [15–20] also has few shortcomings. To illustrate, the hydrogenation of phenol with hydrogen generated from the APR of methanol or ethanol was carried out in stainless steel reactor at very high temperature (217 °C), 3.5 MPa argon pressure and uses bimetallic catalyst (Pd-La₂O₃) [15,16]. The phenol hydrogenation using formic acid on Pd/C was carried out in pressure reactor under specific 3 bar N₂ pressure and specific N₂ pressure (3 bar) found necessary to achieve high phenol conversion [17]. Further similar phenol hydrogenation using formic acid performed under open atmosphere (without N₂ pressure) resulted into incomplete reaction (60% conversion) and reach to plateau; which further never lead to completion even with excess amount of reagent (3–10 equiv.) [17]. Authors assumed that some of the hydrogen has evolved out under open atmosphere which was responsible for incomplete phenol hydrogenation [17].
The phenol hydrogenation using sodium formate as hydrogen donor on Pd/C in closed reaction tube under microwave irradiation at 80 °C revealed complete phenol conversion and high cyclohexanone selectivity [18]. However, when phenol hydrogenation was carried out using conventional heating (instead of microwave) at 80 °C; low conversion was observed (1%) even after few hours (5 h) [18]. Therefore, microwave effect found to be specific and necessary for effective phenol hydrogenation. The phenol hydrogenation using sodium formate on Pd-PANI/CNF as catalyst shows high conversion consistently as in closed conditions as well as at atmospheric pressure [19]. However, polymer (PANI) grafting on Pd/CNF is necessary because phenol hydrogenation using only Pd/CNF shows relatively low conversion (72%) and reduced cyclohexanone selectivity (81%). Therefore, pre-requisite complex synthesis of supporting material PANI/CNF using polymerization of corresponding aniline in carbon nanofibers (CNF) suspension involves additional synthesis steps, economical cost and hazardous chemicals [19]. In order to make industrially important phenol hydrogenation to cyclohexanone as chemist friendly or sustainable chemical transformation, it is necessary to minimize above shortcomings.

Recently, our research group has demonstrated that water activated through reducing metals (Zn, Mg) act as green and alternative hydrogen source for sustainable catalytic transfer hydrogenation (CTH) of organic molecules [21,22]. We have revisited the catalytic transfer hydrogenation of phenol using potassium formate as a benign H₂ source and Pd/C as heterogenous catalyst under aqueous conditions and open atmosphere (atmospheric pressure). In this context, we report herein one pot, selective phenol hydrogenation to cyclohexanone under open atmosphere without the need of specific equipments (autoclave or microwave etc.), closed conditions or specific pressure conditions and specific catalyst synthesis (Scheme 1). Potassium formate as hydrogen source in an organic transformation has been well known in the literature [23]; however the phenol hydrogenation using potassium formate as hydrogen source has been not studied in the past.

2. Experimental

2.1. General

Chemicals were purchased from commercial firms (Aldrich) and used without further purification. Reactions were performed in a round bottom flask. GC analyses were performed using Focus GC from Thermo Electron Corporation, equipped with low polarity ZB-5 column. The NMR (¹H and 13C) spectra were recorded in CDCl₃ and D₂O with Bruker DRX-400 instrument in CDCl₃. The Transmission Electron Microscope (TEM) studies of Pd/C catalyst were done in a Tecnai F20 G2 instrument (FEI). The palladium (Pd) content of product was determined by an Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) Spectrometer (Agilent 7500 cx).

2.2. Experimental procedure for gram scale phenol hydrogenation to cyclohexanone:

In a typical reaction, phenol (2 g, 21.3 mmol), 0.9 g of 10 wt.% Pd/C (0.43 mmol), potassium formate (7.15 g, 85 mmol) and deionized water (20 mL) were introduced into 100 mL round bottom flask. Reaction mixture was subjected to heating at 90 °C for 6 h with continuous stirring. At the end of reaction, the reaction flask was allowed to come at room temperature. The product cyclohexanone was extracted with diethyl ether [25 + 25 + 10 mL] followed by drying with sodium sulphate, filtration using Whatman paper and analyzed by GC. The GC analysis shows >99% of phenol conversion to cyclohexanone. The residue after solvent (diethyl ether) evaporation affords the desired cyclohexanone product (isolated yield = 94%) as colorless liquid. The product cyclohexanone was confirmed through standard injection to GC and ³¹H NMR.

2.3. Recovery and reuse of Pd/C catalyst

After the aqueous–organic reaction work up, catalyst Pd/C dispersed in aqueous phase was filtered through Whatman filter paper. The catalyst Pd/C remains as residue on the filter paper washed with diethyl ether (5 mL), dried in the air and reused as such for further recycling experiments under the similar optimized reaction condition (Table 4, entry 2).

3. Results and discussion

In order to optimize reaction condition for higher phenol conversion and excellent selectivity of desired cyclohexanone various experimental parameters were explored. Initially, we have optimized reaction time for phenol hydrogenation while other reaction parameters [phenol (2.1 mmol), potassium formate (4 eqv.), 10 wt.% Pd/C (2 mol%), water (10 mL) and 100 °C temperature] were kept constants (Table 1). Since reaction mixture containing water, organic substrate and products is non-homogeneous; it has difficult task to monitor the reaction kinetics (reaction rate with time) in a single reaction. Therefore we have carried out separate reactions for different time period to optimize reaction time (Table 1). The phenol hydrogenation showed 85% conversion after 5 h with excellent selectivity (Table 1, entry 1). After 6 h, excellent phenol conversion and cyclohexanone selectivity (>99%) was observed and it was found as optimize reaction time for phenol hydrogenation under given conditions (Table 1, entry 2). A reduction of reaction time less than 6 h, provided incomplete conversion (85% in 5 h) while excess time (14 h) allows conversion of desired cyclohexanone to cyclohexanol and thereby decreases cyclohexanone selectivity (Table 1, entries 3 and 4). It is challenging task in phenol hydrogenation to achieve high cyclohexanone selectivity especially at high conversion [24,25]. In the present system, we were successful to achieve excellent phenol conversion and cyclohexanone selectivity simultaneously under simple and mild reaction conditions (Table 1, entry 2).

Subsequently, we turned our attention to examine the effects of the other reaction parameters on the present reaction outcome. Reactions at 80 °C or above it were provided complete phenol conversion and excellent cyclohexanone selectivity without any other external driving force such as external pressure (Table 2, entries 1–4). When the temperature decreased at or below 70 °C, phenol conversion starts slightly decreasing (Table 2, entry 5). At 60 °C,
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