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Highly efficient and selective catalytic hydrogenation of acetylene in *N*,*N*-dimethylformamide at room temperature

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ABSTRACT

The removal of acetylene from ethylene streams is a key requirement in polymer industry. Two approaches, based on either catalytic selective hydrogenation or isolation using suitable solvents, have driven considerable scientific research in academia and industry. These two approaches exhibit their own specific advantages, but an acetylene-removal strategy combining all these distinct features was still missing. Here we show that acetylene dissolved in *N*,*N*-dimethylformamide (DMF) can be selectively hydrogenated to ethylene (>90%) by Pd nanoparticles easily prepared *in situ*. By this strategy, which was optimized for several parameters, we could attain a catalytic activity higher by a factor of 2.7 orders of magnitude than that of the currently used industrial method. This strategy was successfully tested on a mixture of acetylene and ethylene. Importantly, the process here described is performed at room temperature and under additive-free conditions. This approach may thus provide a new methodology for selective acetylene-hydrogenation purposes.

1. Introduction

Selective hydrogenations are very important reactions in organic synthetic chemistry, widely used particularly in pharmaceutical and petrochemical processes. A fundamental material for polymer synthesis is ethylene, whose industrial production is normally carried out by the steam-cracking method. This process, however, is unavoidably accompanied by formation of acetylene. Albeit present in small amount, acetylene needs to be removed from the ethylene streams because its presence would severely impact the product purity as well as deactivate the polymerization catalyst in the downstream of polymer production [1]. To purify ethylene streams from acetylene, catalytic hydrogenation of acetylene to ethylene is regarded as the most efficient method [2,3]. The selectivity of the heterogeneous catalyst thus plays a pivotal role, particularly because overhydrogenation to form ethane and/or coupling reactions must be avoided. The catalyst should also maintain high reactivity and stability during the hydrogenation process. Over the last few years, several ways to prepare catalysts ideally matching these requirements have been explored [2–21]. Typical catalysts for the hydrogenation of alkynes are Pd-based materials. These catalysts have long been recognized to display remarkable activity for acetylene hydrogenation, but yet with limited ethylene selectivity [1,4,5]. Recent research indicates that the selectivity of acetylene hydrogenation strongly depends on the catalyst phase. For example, if hydrogen is dissolved in the bulk, formation of hydrides occurs and unwanted overhydrogenation species become the favored products. On the other hand, carbides in the form of carbonaceous deposits are selective toward ethylene [6–8]. Density-functional calculations have attributed selectivity to a competition between the energy for the desorption of ethylene and the activation free energy for further ethylene hydrogenation [1]. It is, therefore, not surprising that these observations led to proposing a plethora of alternative catalysts. Various additives, such as Ag [9,10], Au [11], Cu [5,12], Ni [13], Zn [14], B [15], have been incorporated to form bimetallic Pd catalysts, and intermetallic compounds (IMC) based on the site-isolation concept, such as Pd–Ga [3] and Pd–Zn [16], have been devised and developed. The purpose was to decrease the adsorption energy of ethylene on the catalyst surface and limit the strong activity of Pd, thereby attaining higher ethylene selectivity by preventing overhydrogenation. More recently, the need of reducing the costs associated with Pd-based materials has led to develop catalysts composed by nonprecious metals and even nonmetallic materials, such as Ni–Zn

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[1,17], Cu–Fe–Ni [18], $Al_{13}Fe_4$ [19], $Al_{13}Co_4$ [20] and graphenes [21]. All of them show remarkable ethylene selectivity and could be used, in principle, to replace the precious metals currently used. Although these catalysts exhibit their own virtues, the sheer number of reports on this topic suggests that no single catalyst can be considered as sufficiently performing for acetylene hydrogenation. It also is worth noting that the most interesting outcomes have been often achieved by carrying out the reaction under high temperature and pressure conditions (as high as 200 °C and 20 bars). Losses caused by generation of undesired ethane and oligomers, as well as complications associated with the preparation of the catalyst, are not uncommon. All these factors contribute to make the catalytic hydrogenation of acetylene not devoid of problems.

To purify ethylene streams from traces of acetylene, the isolation method furnishes another effective strategy. Depending on the isolation medium, two types of approach can be employed. The first method employs a solid adsorbent, such as activated carbon, zeolites or metal–organic frameworks (MOFs), and mainly relies on the difference between the interaction energy of C–C triple and double bonds on the adsorbent surface [22–25]. The second approach is based on the use of a liquid absorbent in which the solubilities of acetylene and ethylene are sufficiently different to allow for a complete separation of acetylene from the ethylene streams [26,27]. Acetone and *N*,*N*-dimethylformamide (DMF) are solvents widely used in industry for storage/transport of acetylene and to isolate acetylene from ethylene streams. It is worth noting, however, that whereas the sought result can be achieved by adopting either isolation method, the so-separated acetylene is wasted rather than converted into a valuable product, such as ethylene itself.

Selective hydrogenation of alkynes in liquid phase is an important topic addressed for decades, starting from the Lindlar reduction [28,29]. Development of heterogeneous catalysts has evolved from the original Lindlar catalyst to the most recent nanosized or metallated organic polymer materials [29,30]. Despite the high selectivity achieved toward alkenes, few studies of the selective acetylene hydrogenation in liquid phase have been carried out. In this regard, we showed that the electrochemical reduction of acetylene in DMF furnishes an interesting strategy [31]. In addition, novel solid catalysts modified with an ionic liquid layer proved to enhance ethylene selectivity slightly, but at the expense of catalyst activity [32,33]. Very recently, acetylene hydrogenation with high ethylene selectivity was achieved in *N*-methylpyrrolidone (NMP) using Pd supported on silica [34,35] or the graphite-like material Sibunit [36] at quite high temperatures (90–100 °C). Here we describe a strategy, combining the advantages of both heterogeneous catalysis and the isolation approach, in which acetylene dissolved in DMF is efficiently and selectively hydrogenated to ethylene by *in situ* prepared Pd nanoparticles (NPs), under additive-free conditions and, very importantly, at ambient temperature.

2. Experimental

2.1. Catalyst preparation

The PdNPs (1.0 mol%, with respect to the amount of acetylene) were prepared by adding aqueous $NaBH_4$ (3.0 equiv) dropwise to a DMF solution containing $Pd(OAC)_2$ (0.715 μmol for 20 ml vial or 14.3 μmol for 250 ml flask reactor), under magnetic stirring conditions. The solution turned immediately black as a consequence of reduction to form Pd^0 (Eq. (1)):

$$2Pd^{2+} + BH_4^- + 3H_2O \rightarrow 2Pd^0 + H_2BO_3^- + 4H^+ + 2H_2 \quad (1)$$

2.2. Catalysis tests

This study was conducted by carrying out the hydrogenation reaction in two different reactors. The first was a vial reactor, in which the catalytic test and the reaction conditions investigation for PdNPs were carried out in a 20 ml screw top headspace vial placed in a shaker (300 rpm, 25 °C). Generally, a fixed amount of acetylene (0.0715 mmol) was injected into the prepared catalyst solution, followed by addition of the appropriate $NaBH_4$ aqueous solution to form a final 10 ml DMF–water solution.

The second reactor was a 250 ml flask, which was mainly utilized to magnify the reaction scale. After addition of $Pd(OAC)_2$ and $NaBH_4$, the solution was stirred for another half an hour until hydrogen evolution ceased, and then a determined amount of acetylene (1.43 mmol) was injected into the reactor now containing a 100 ml DMF–H_2O solution (7:3, V:V) and 1.0 mol% PdNPs. After distribution balance of acetylene, a stoichiometric amount of $NaBH_4$ (1.0 equiv) or H_2 (1.14 or 2.86 equiv) was added to trigger the catalytic hydrogenation reaction. For each heterogeneous catalysis condition, three parallel experiments were conducted to ensure the repeatability of experiment. Two control experiments, namely one in the absence of catalyst and the other in the absence of $NaBH_4$, were carried out simultaneously. During the acetylene hydrogenation process, gas samples were withdrawn at fixed time intervals, using a tight gas syringe, and analyzed with a Shimadzu QP2010 ultra gas chromatograph (GC) equipped with a mass spectrometer (MS). The MS was scanned from 12 to 100 m/z every 80 ms, where the sum of these ions is referred to as the total ion count (TIC). Quantification of the gas components was performed by integrating the TIC and comparing the peak areas with the calibration curves obtained with mixed gas standards (31.7% acetylene, 31.9% ethylene, 14.9% ethane, 5.2% methane, 2.03% 1-butene, 1.99% *n*-butane, 1.99% 1,3-butadiene and 2.00% propane; argon was used as the balance gas). Acetylene was handled as a gas containing 35.0% acetylene and 65.0% argon. The acetylene and mixed gas standards were prepared using gasses (the purities of these gas were >99.99%) purchased from Airichem Specialty Gases & Chemicals Co., Ltd. (Dalian, China). DMF (from Sigma Aldrich, >99.8%, HPLC grade) and all other chemicals (analytical grade) were used as received. The aqueous solutions were prepared with Millipore-Q water (18.2 MΩ).

3. Results and discussion

PdNPs were synthesized from a stirred solution of $Pd(OAC)_2$ in DMF to which aqueous $NaBH_4$ was added dropwise at room temperature. A black color, indicative of the formation of PdNPs *via* two-electron reduction of Pd(II), immediately formed and a gas evolved. For the sake of characterization, the NPs were separated from the reaction solution by centrifugation, washed with water and then ethanol, and finally analyzed for size and composition by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). The so-prepared PdNPs have an average size of 7.6 ± 2.1 nm, as illustrated in the TEM image and histogram of Fig. 1A and inset. The PdNPs display a quite spherical shape, and the TEM images show no obvious aggregation phenomena. The high resolution TEM (HRTEM) image in Fig. 1B highlights the crystalline nature of these PdNPs. The interplanar spacing, observed from the lattice fringes, is 0.227 nm (inset), which agrees well with the (1 1 1) lattice-spacing of face-centered cubic (fcc) Pd [37,38]. The EDS composition analysis further points to the purity of the so-prepared PdNPs.

For the catalysis experiments, we used the PdNPs directly in their preparation vial, after hydrogen release exhausted. A typical reaction was carried out as follows. The reaction vessel was a