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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 non-precious 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)):

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

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

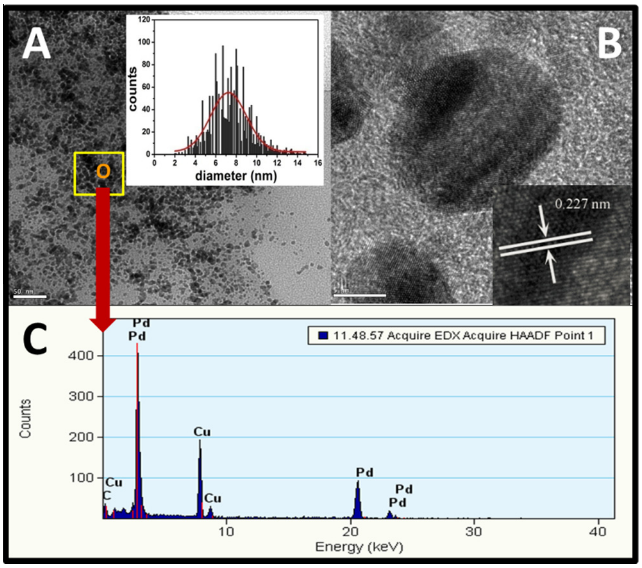

Fig. 1. (A) TEM image of PdNPs and (inset) histogram showing the size distribution for the Pd colloid. (B) HRTEM image of PdNPs and the crystalline PdNP with resolvable atomic lattice. (C) EDS spectrum corresponding to the zone highlighted is shown in panel.

20 ml screw top headspace vial placed in a shaker (300 rpm, 25 °C). A fixed amount of acetylene (0.0715 mmol) was injected into the Pd solution, followed by addition of the appropriate amount of $NaBH_4$ aqueous solution to form a final 10 ml DMF–water solution. Beside the actual catalytic runs, we carried out two control experiments and found that in both cases the concentration of acetylene remained constant: whereas in one experiment there was no catalyst, in the second experiment we did not add $NaBH_4$. The latter allowed us to check that very small amount of dissolved hydrogen resulting from the excess of $NaBH_4$ (ca. 0.05 equiv relative to acetylene) used for the preparation of the PdNPs does not contribute to acetylene hydrogenation.

Fig. 2A refers to acetylene hydrogenation conducted in the presence of 1.0 mol% Pd and 1.0 equiv $NaBH_4$ in 10 ml DMF–water solution (7:3, V:V). Reduction to ethylene occurs promptly and proceeds with high acetylene conversion (>80%) and an ethylene selectivity of ca. 90% in 10 min (Fig. 2A). As time increases, the occurrence of side reactions forming ethane and C4 compounds as a result of overhydrogenation and C–C coupling reactions, respectively, can be observed. No ethane forms until an acetylene-to-ethylene conversion of >80% is achieved and thus that ethylene hydrogenation only occurs when the acetylene concentration drops to low values. These results indicate that there is a significant difference in the rates for the first and second hydrogenations, and therefore, that overhydrogenation, which after 2 h yields 38% ethane, can be effectively controlled by adjusting the reaction time. Formation of C4 compounds starts from the beginning of the reaction but levels off at 10% (Fig. 2A); no heavier hydrocarbons were observed throughout the whole studies. It thus appears that the generation of C4 compounds is inevitable and originates from acetylene. This is in keeping with previous studies about the catalytic hydrogenation of acetylene in gas phase, in which formation of C4 compounds was attributed to coupling reactions of acetylene [6,17]. It should be noted, however, that whereas in the gas phase the coupling by-products may accumulate on the catalyst surface, thereby leading to its deactivation, in DMF the catalyst is expected to be stable due to the good solubility of C4 compounds and oligomers. To test this expectation, we ran recycle experiments, which will be described below.

The reaction conditions play a significant role on the catalytic performances in both acetylene conversion and ethylene selectivity. We tested the effects of the ratio between DMF and water, the dosage of PdNPs, and the amount of $NaBH_4$. Fig. 2B illustrates the most salient results obtained after 10 min. Compared to the other factors, the DMF-to-water ratio displays the largest effect. The general trend (10 min runs) is that as the water content decreases, acetylene conversion first increases, then peaks at a ratio of 7:3 (>80%), and finally undergoes a sudden decrease until no reaction at all takes place in formally anhydrous DMF. Ethylene selectivity remains initially constant at ca. 90% and then, for ratios larger than 7:3, starts decreasing in a similar manner. When the reaction is protracted to 2 h (data not shown in Fig. 2B), whereas the 5:5 and 6:4 ratios allow for quantitative conversion of acetylene, the performance decreases to ca. 90%, 55%, 36% and 0% for the 7:3, 8:2, 9:1 and 10:0 ratios, respectively; at the same time, the ethylene selectivity undergoes a sharp decrease due to overhydrogenation and C–C coupling reactions.

These trends can be explained by considering both the hydrolysis of $NaBH_4$ and the reactivity of the unsaturated bonds of acetylene and ethylene. In the catalysis experiments, the main role of $NaBH_4$ is to provide hydrogen through its hydrolysis reaction, $NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2$ [39], thus pointing to water as indispensable for the hydrogenation to occur. Large DMF-to-water ratios would to some extent limit the hydrolysis of $NaBH_4$ but also

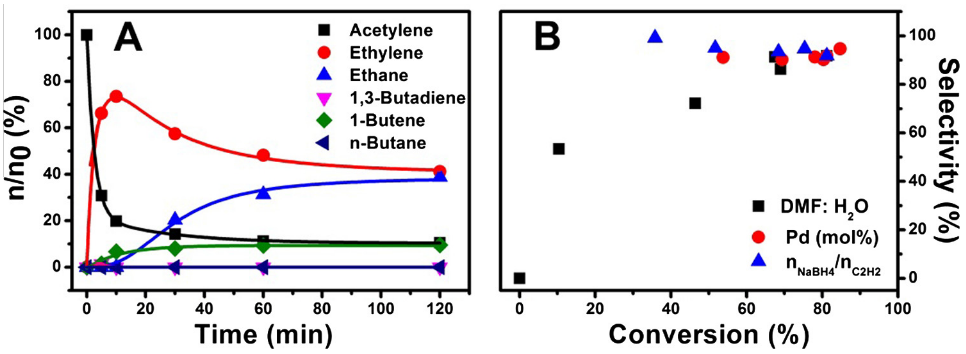

Fig. 2. Catalytic results of the hydrogenation of acetylene. (A) Reaction conditions: 1.0 mol% PdNPs, 0.0715 mmol of acetylene dissolved in 10 ml DMF–water solvent (V:V, 7:3), $NaBH_4$ (1.0 equiv), 25 °C, 300 rpm, 2 h. For the sake of better comparison, the amounts of C4 compounds (*n*) were doubled in view of the coupling reaction of C2 compounds. (B) Reaction conditions tested (10 ml solvent, 25 °C, 300 rpm, 10 min): (i) DMF-to-water ratio (V:V, squares, left to right: 10:0, 9:1, 8:2, 5:5, 6:4, 7:3; 1.0 mol% Pd, 1.0 equiv $NaBH_4$); (ii) PdNPs dosage (circles, left to right: 0.1, 0.5, 5.0, 2.0, 1.0, 10.0 mol%; DMF-to-water ratio of 7:3, 1.0 equiv $NaBH_4$); (iii) $NaBH_4$ amount (triangles, left to right: 0.25, 5.0, 2.0, 0.5, 1.0 equiv; DMF-to-water ratio of 7:3, 1.0 mol% Pd). Please note that three experimental data pertaining to conditions (i–iii) overlap: DMF-to-water ratio at 7:3, Pd loading at 1.0 mol%, and $NaBH_4$ amount at 1.0 equiv.

affect the solubility of by-product (inorganic sodium salts). These factors would cause insufficient hydrogen availability and partial deactivation of the active sites on PdNPs by inorganic salts (see the recycle experiment below), thus resulting in a poor acetylene hydrogenation performance and eventually no reaction in pure DMF. Under these conditions, low ethylene selectivity in 10 min is obtained as a consequence of limited acetylene conversions, but with almost constant formation of C4 compounds for all DMF-to-water ratios (except 10:0). On the other hand, lower ratios (*e.g.*, 6:4 and 5:5) favor the generation of hydrogen, which may affect the reaction outcome from different viewpoints, especially during the first minutes of the reaction. First, it may detriment acetylene adsorption, and thus its conversion, owing to significant dissociative adsorption of hydrogen on the Pd surface. Second, excess adsorbed hydrogen may eventually favor overhydrogenation at the expense of ethylene selectivity. Third, the actual amount of DMF is the factor determining the solubility of acetylene [26,27], which implies that decreasing its amount eventually affects the isolation capability of the reaction medium. On these grounds and considering that at a DMF-to-water ratio of 7:3 a very high solubility of acetylene can be attained (at distribution balance, we found that repartition between gas and solution phases is 6:94), this specific ratio provides the best combination for attaining high acetylene conversion, ethylene selectivity, and acetylene solubility, and it will thus be used consistently in the following experiments. It is finally worth noting that the major C4 compound, 1-butene, only builds up in solution up to a maximum concentration of ca. 5% and ca. 10% after 10 min and 2 h, respectively, regardless of the DMF/water ratio. This further confirms that C–C coupling appears as inevitable, but still within an acceptable range.

To evaluate the effect of the PdNPs dosage on the efficacy of acetylene hydrogenation, we tested different amounts: 0.1, 0.5, 1.0, 2.0, 5.0, and 10.0 mol%. Fig. 2B shows that the dosage of Pd does not produce any obvious effect on the ethylene selectivity in the presence of at least 1.0 equiv of $NaBH_4$, and the ethylene selectivity remains constant to >90% in 10 min. Small dosages of Pd, such as 0.1 and 0.5 mol%, result in a slight decrease of acetylene conversion, 54% and 69%, respectively, compared with 81% of 1.0 mol% addition. For Pd dosage beyond 1.0 mol%, no significant changes in acetylene conversion (ranging from 78% to 84%) occur. In these conditions, only traces of ethane and *n*-butane are detected. By extending the reaction time to 2 h, whereas the acetylene conversion increases to 71% and 80% for 0.1 and 0.5 mol% PdNPs, respectively, and for PdNPs beyond 1.0 mol% becomes over 90%, the ethylene selectivity consistently undergoes a remarkable decline due to the overhydrogenation and C–C coupling reactions. It appears that 1.0 mol% of PdNPs provides sufficient active sites to acetylene and hydrogen for the hydrogenation reaction to occur smoothly. In 10 min, we did not observe any obvious trend in terms of acetylene conversion and ethylene selectivity for Pd dosage beyond 1.0 mol%. After 2 h, however, an increase of Pd dosage causes a more substantial formation of ethane (ranging from 38% to 48%) and butane (in a range of 0.5–2%), an observation that could point to the presence of an excess of Pd active sites in the reaction mixture. Overall, these results suggest that a small dosage of Pd is indeed sufficient for triggering the acetylene hydrogenation efficiently, which is a very significant observation in view of the cost of this metal. In the following, we will focus on the use of 1.0 mol% as the reference amount of PdNPs.

The amount of $NaBH_4$ was also examined, and the results are shown in Fig. 2B. By increasing the amount of $NaBH_4$ from 0.25 to 1.0 equiv, the acetylene conversion increases from 36% to 81% in 10 min, while the ethylene selectivity is quite constant at ca. 90%. After 2 h, the acetylene conversion tends to stabilize at 45%, 84% and 90% for 0.25, 0.5, and 1.0 equiv addition of $NaBH_4$, respectively. However, whereas the ethylene selectivity is still over 90% for the first two concentrations of $NaBH_4$, for 1.0 equiv it decreases to 46%, with substantial ethane formation. Finally, if the amount of $NaHB_4$ is further increased to 2.0 up to 5.0 equiv, the acetylene conversion decreases to 68% and 52%, respectively, in 10 min, but still with ca. 90% of ethylene selectivity. Noteworthy, whereas after 2 h the acetylene conversion increases to 88% and 78% for 2.0 and 5.0 equiv $NaBH_4$, the ethylene selectivity undergoes a sharp decline to 44% and 39%, respectively, accompanied by significant formation of ethane. Overall, these results indicate that at low $NaBH_4$ dosage the acetylene hydrogenation is controlled by insufficient availability of hydrogen, resulting in limited acetylene conversion. On the other hand, an amount larger than 1.0 equiv does not favor conversion and selectivity, most likely because of the large release of hydrogen that can affect the adsorption of acetylene, as well as the problems associated with the increase of inorganic sodium salts from $NaBH_4$ hydrolysis and resulting deactivation of the Pd active sites (see the recycle experiment below). The ethylene selectivity results further suggest that acetylene hydrogenation occurs in a sequential manner, and that overhydrogenation only takes place under the conditions of almost depletion of acetylene and in the presence of excess hydrogen. On these grounds, for the following experiments we thus used 1.0 equiv $NaBH_4$.

To further test the scope and efficacy of this hydrogenation approach, we carried out the reaction on a larger scale and carried out recyclability experiments. We used a 250 ml flask containing 100 ml DMF–water solution (V:V, 7:3) and 1.0 mol% PdNPs as the catalyst; 1.43 mmol acetylene was then injected. Hydrogenation started upon addition of 1.0 equiv $NaBH_4$, under vigorous magnetic stirring. We found that 82% of acetylene was converted in 10 min with 90% of ethylene selectivity, in excellent agreement with the previous vial experiment. Interestingly, whereas after 2 h the acetylene conversion stabilizes at around 90%, as opposed to the outcome observed in the smaller scale reaction the ethylene selectivity remains at 89% with only trace of overhydrogenation product formation. We speculate that this positive outcome could be due to more efficient mixing conditions (3000 rpm), in the sense that as ethylene forms it is quickly removed from the reaction mixture because of its poor solubility and weak adsorption affinity onto PdNPs, resulting in a high selectivity. As a matter of fact, we verified that when ethylene is injected into a DMF–water solution (7:3, V:V), ethylene is then found in the gaseous phase over the solution but not in the latter. These results further confirm the efficacy of this novel acetylene hydrogenation method, and suggest that proper adjustment of the actual experimental conditions, such as stirring speed and headspace volume, may be quite important in designing a pilot-tests reactor.

The possibility of recycling the whole system was tested as follows. Once the hydrogenation was complete, the sealed system was temporarily unfolded to discharge excess pressure, and then new acetylene was introduced (1.43 mmol), followed by addition of fresh $NaBH_4$ (1.0 equiv) and test of the hydrogenation outcome. As shown in Fig. 3A, this process was repeated 5 times: whereas an evident decline of acetylene conversion is detectable for the first two cycles, afterward conversion tends to stabilize at ca. 30%. Noteworthy, if the reaction time is extended to 2 h, the conversion can still reach ca. 80% in the last cycle. Despite low acetylene conversion in the last cycles, high ethylene selectivity (beyond 80%) is nonetheless achieved throughout the whole recycle experiments. It is finally worth noting that upon recycling we observed agglomeration phenomena, in the sense that the dark PdNPs containing solution gradually become transparent (Fig. S4B). In this regard, the EDS results (Fig. S1) confirmed the co-existence of sodium in the particles collected after the recycling experiments. This could explain the deactivation of the PdNPs interacting with the inorganic sodium salts during the continuous addition of $NaBH_4$. These results as well as the sedimentation of PdNPs during recycle tests

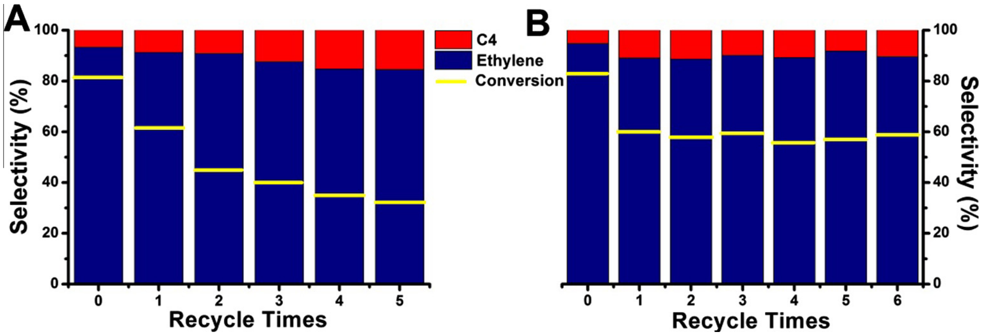

Fig. 3. Recycle tests of PdNPs for acetylene hydrogenation. (A) $NaBH_4$ as hydrogen source. Reaction conditions: 1.0 mol% PdNPs, 1.43 mmol acetylene dissolved in 100 ml DMF–water solvent (V:V, 7:3) each cycle, 1.0 equiv $NaBH_4$, 25 °C, 3000 rpm, 10 min. (B) Direct use of H_2. Reaction conditions: 1.0 mol% PdNPs, 1.43 mmol acetylene dissolved in 100 ml DMF–water solvent (V:V, 7:3) each cycle, 2.86 equiv H_2, 25 °C, 3000 rpm, 10 min.

are detailed in the Supporting Information. After recycling, the PdNPs were washed with excessive water and ethanol, and then reused for another acetylene-hydrogenation run. The results demonstrate that the catalytic activity is fully recovered, and further TEM–EDS results (Fig. S2) indicate the disappearance of sodium after water washing. To further confirm that sodium salts cause deactivation of the PdNPs, $NaBH_4$ was replaced by pure H_2 gas as the hydrogen donor (see below). To test the stability of the catalyst, the PdNPs (1.0 mol%) were prepared and kept in a 7:3 DMF–water solution for 10 and 30 days. In both cases, upon addition of acetylene and 1.0 equiv $NaBH_4$, whereas after 10 min we observed no evident changes in either acetylene conversion (>80%) or ethylene selectivity (>90%), after 2 h ca. 50% of ethylene selectivity with substantial ethane formation was still obtained. In addition, freshly prepared PdNPs displays a remarkable stability and well dispersion in DMF solution even after 4 h, as shown in Fig. S4A. These results plus the reusable characteristic thus point to a very good stability of these PdNPs in the developed approach.

This is the first example of PdNPs that utilize $NaBH_4$ as hydrogen donor and in which selective hydrogenation of acetylene is carried out at ambient temperature under additive-free conditions. In fact, whereas reduction of alkynes by $NaBH_4$ has been already reported, the process was found to suffer from poor alkene selectivity or required a surfactant as an additive [29,40,41]. The results here described may conceivably shed some light onto the selective hydrogenation of other alkynes to alkenes, reactants of paramount importance in manufacturing petrochemicals and fine chemicals. On the industrial scale, acetylene hydrogenation is carried out using directly hydrogen gas, particularly because H_2 is considerably present in the pyrolysis streams and its amount with respect to acetylene can be changed on purpose, especially in the "tail-end" selective hydrogenation (TESH) process [2,34,42]. The following experiments thus focus on the use of pure H_2 as hydrogen donor to test the catalytic performances of the PdNPs and the isolation strategy.

Pure H_2 (2.86 equiv) was directly introduced into the 250 ml flask, all other conditions being kept unaltered. As expected, this approach also leads to high acetylene conversion (81%) and remarkable ethylene selectivity (94%) in 10 min, accompanied by overhydrogenation and coupling reactions with ethylene selectivity decreasing to 80% after 2 h. However, when the amount of H_2 is lowered to 1.14 equiv, in 10 min the initial acetylene conversion rate decreases to 48%; in 2 h, over 80% acetylene conversion is obtained and, very significantly, ethylene selectivity reaches ca. 98%. These results point to a lower hydrogenation ability when hydrogen is present at low concentration. To gain more insights into this selectivity aspect, we tested other H_2 amounts in the range from 0.5 to 4.0 equiv. The results clearly show that a high H_2 pressure results in a high acetylene conversion in 2 h, but accompanied by significant overhydrogenation reactions; in 10 min, however, over 90% ethylene selectivity was always observed. This is in keeping with a previous study, concerning the selective hydrogenation of internal and terminal alkynes by PdNPs, in which the selectivity toward alkene or alkane was sensitively affected by the hydrogen pressure [43]. Overall, these results show that H_2 gas can be directly and efficiently used as hydrogen donor. They also confirm our conclusion that the conversion of acetylene to ethane proceeds in a sequential manner in which ethane is produced only after most acetylene is transformed into ethylene and in the presence of excess hydrogen. Similar results, concerning the hydrogenation of 1-pentyne, have been observed in a recent work [44]. These observations suggest that overhydrogenation can be controlled by limiting the amount of H_2 and/or the reaction time, in keeping with a favorable rate difference for acetylene and ethylene hydrogenation and a favorable adsorption-energy difference on the Pd catalyst surface.

Another major characteristic of this hydrogenation process is the possibility of recycling the contents of the whole reaction mixtures. The outcome of the recycle experiments (Fig. 3B, 2.86 equiv H_2) shows that acetylene conversion slightly decreases in the first cycle and then stabilizes at ca. 60% during the following cycles, while ethylene selectivity remains consistently at 90%. No noticeable change of the TEM images, in terms of size and lattice pattern of the NPs, and no obvious agglomeration phenomena were observed for the Pd catalyst after recycling (as shown in Fig. S3). In addition, essentially no changes occurred in the sedimentation curves of PdNPs during the recycle tests, as shown in Fig. S4C. These results not only show that the catalyst is stable but also bring further evidence that deposition of inorganic sodium salts onto the PdNPs is the most plausible cause for the deactivation of the catalyst when $NaBH_4$ is used as a hydrogen source. The outcome of the recycle experiments also excludes that deactivation of Pd is associated with the coupling reactions, although minimum formation of C4 compounds is consistently observed. The potential applicability of the developed approach was demonstrated using a mixture of acetylene and ethylene (1:9, *n*:*n*) in the presence of 1.0 mol% Pd and 2.86 equiv H_2 in a 250 ml flask. The selectivity in acetylene hydrogenation (78% acetylene conversion with more than 90% ethylene selectivity in 10 min) was in excellent agreement with the aforementioned results. By extending the reaction time to 2 h, the acetylene conversion rate improved to 90%, whereas ethylene selectivity decreased to ca. 50%. Interestingly, whereas considerable ethylene and excessive H_2 were present in the mixtures, no significant overhydrogenation was observed, which would indicate that free ethylene is not involved in the hydrogenation reaction. This could be accounted for by considering the poor solubility of ethylene in DMF as well as its lower adsorption affinity onto the PdNP surface than acetylene. We thus speculate that overhydrogenation occurs from the ethylene just obtained from acetylene but not yet desorbed from the catalyst surface. At difference from experiments carried out with pure acetylene, significant ethylene is found in the headspace. This may detriment diffusion of the newly formed ethylene from the solution to the headspace, thereby leading to more ethane formation for the reactions based on the acetylene–ethylene mixtures. Overall, these results thus suggest that highly efficient and selective acetylene hydrogenation can be attained even in the presence of considerable ethylene, and this further confirms the feasibility of the proposed approach.

The observed high selectivity for acetylene hydrogenation and stability of the so-prepared PdNP catalysts in DMF are quite intriguing. Compared to the currently used industrial method for the gas-phase catalytic hydrogenation of acetylene [45], our approach exhibits a much better hydrogenation reactivity (by a factor of 487) and a higher selectivity (>90% vs. ~50%) (details are provided in the Supporting Information). This points to the very significant potential impact of this novel approach. One possible explanation is due to the formation evidenced by HRTEM, of the Pd(1 1 1) facet, which is generally acknowledged as the best surface for catalytic reactions [37,38]. Moreover, the high dispersion and stability of the PdNPs in DMF are also favorable to enhance the catalytic performance. In this context, we note that the use of DMF as a reaction medium for the synthesis of metal NPs was reported previously [46,47], with DMF normally used as both the solvent and the reductant in reactions conducted at high temperatures. Whereas both types of hydrogen donor (direct hydrogen donor, H_2, and indirect hydrogen donor, $NaBH_4$) enable an efficient conversion of acetylene to ethylene, some differences between the hydrogenation mechanisms are possible. At variance with H_2, the hydrogen source is not as straightforward when $NaBH_4$ is used, as hydrogen may originate from $NaBH_4$ or H_2O, or both. It is widely known that Pd catalysts may enable the hydrolysis of $NaBH_4$ and release hydrogen gas, a process where palladium hydride (Pd-H) is first formed as an intermediate [40,48]. As acetylene is also readily adsorbed on the Pd surface, this could explain the remarkable efficiency in acetylene hydrogenation when $NaBH_4$ is used as a hydrogen donor. Pd-H can also exchange with H_2O [48], resulting in the possibility that the hydrogen source is not only $NaBH_4$. According to a recent study [29], water plays no role in providing hydrogen for the hydrogenation of non-conjugated alkynes by PdNPs; instead, for the conjugated ones, the hydrogenation atoms were found to come from both $NaBH_4$ and H_2O. Owing to the excess $NaBH_4$, quenching of Pd-H thus yields H_2. Similarly, when hydrogen gas is directly used as a hydrogen donor, the first step is hydride formation on the Pd surface [5,44]. Whatever the hydrogen source, palladium hydride is thus expected to play an important role in both the hydrolysis (for $NaBH_4$) and the hydrogenation routes. The electronegativity of Pd makes the Pd-H bond polar [48]. Owing to the electrophilicity of alkynes, polar hydrogen species are more reactive toward alkynes than alkenes [49], thus leading to the high ethylene selectivity. The observed excellent ethylene selectivity for acetylene hydrogenation may thus arise from a combination of factors, such as particularly the polar/atomic hydrogen species formed on the Pd catalyst surface, the relative solubility of acetylene and ethylene in DMF, differences in adsorption affinity on the PdNP surface, and a favorable rate difference between the possible hydrogenation processes.

4. Conclusions

The catalysis results here described demonstrate a strategy based on blending the advantages of both the isolation and the heterogeneous catalytic approaches can be successfully applied for the selective acetylene hydrogenation. Acetylene dissolved in DMF can be efficiently and selectively hydrogenated to ethylene at ambient temperature under additive-free conditions, no matter whether hydrogenation is carried out using molecular H_2 or $NaBH_4$ as the hydrogen source. *In situ* easily prepared PdNPs exhibit a strong catalytic activity. Under the several reaction conditions tested, we attained an ethylene selectivity of over 90% and a remarkable activity higher by 2.7 orders of magnitude compared to current industrial catalytic method. Recycle tests point to good stability and high reactivity of the nanocatalysts. This excellent catalytic performance is attributed to a combination of factors including the surface properties of PdNPs and their high dispersibility and stability in DMF solution, a favorable rate difference between the first (acetylene to ethylene) and second (ethylene to ethane) hydrogenation processes, the solubility differences of acetylene and ethylene in DMF, and the relative adsorption affinity of these chemicals on the PdNPs. Considering that the acetylene hydrogenation is a paradigmatic reaction normally catalyzed in gas phase and quite severe temperature and pressure conditions, the method here proposed may conceivably pave a new way for carrying out effective acetylene hydrogenation in liquid phase under mild conditions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.03.028.

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