Nanoparticle Catalysis

Fabrication of Ultrafine Palladium Phosphide Nanoparticles as Highly Active Catalyst for Chemoselective Hydrogenation of Alkynes

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Abstract: Monodisperse palladium phosphide nanoparticles (Pd-P NPs) with a smallest size ever reported of 3.9 nm were fabricated using cheap and stable triphenylphosphine as phosphorous source. After the deposition and calcination at 300 °C and 400 °C, the resulting Pd-P NPs increased in size to 4.0 nm and 4.8 nm, respectively. Notably, the latter NPs probably crystallized with a single phase of $Pd_3P_{0.95}$, which acted as a highly active catalyst in semi- and stereoselective hydrogenation of alkynes. X-ray photoelectron spectroscopy analysis determined a positive shift of binding energy for Pd(3d) in Pd-P NPs compared to that in Pd on carbon. It indicated the electron flow from metal to phosphorus and the larger electron deficiency of Pd in Pd-P NPs, which suppressed palladium hydride formation and subsequently increased the selectivity. Thus, this result may also indicate the applications of Pd-P and other metal-P NPs in various selective hydrogenation reactions.

Selective hydrogenation of carbon-carbon triple bonds is an important route to achieve olefin chemicals, especially for stereospecific products. Among others, noble metals are one type of the most active and versatile heterogeneous catalysts for hydrogenation reactions. Once modified, they can act as ideal selective catalysts. For example, lead poisoned Pd/CaCO₃ named as the conventional Lindlar catalyst,^[1,2] noble metal decorated by self-assembled monolayer (SAM),^[3-6] and Pd-M (M=Cu, Ag, Zn, et al) bimetallic systems^[7-10] have been extensively studied as selective hydrogenation catalysts. However, the use of toxic lead compounds, high cost, and/or decreased activity with respect to these catalysts blocked their practical applications. On the other hand, metal-metalloid alloy nanomaterials were promising catalyst candidates for hydrogenation of acetylene in gas-phase conditions.^[11-13] The interaction between noble metal and metalloid element made the metal

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electronic deficient and also formed a high energy barrier for subsurface chemistry, segregation, and metal hydride formation.^[11,14,15] Nickel phosphide (Ni-P) nanocatalysts were once reported for the chemoselective hydrogenation of alkynes,^[16] however, low reactivity and low Z/E ratio of internal alkenes were observed. Although metal phosphide nanomaterials have been extensively studied in many areas, $^{\left[17\right] }$ the application of Pd-P NPs in selective catalysis is rare. To date, the fabrication of Pd-P NPs was usually carried out using white phosphorus or trioctylphosphine (TOP) as phosphorus source.^[17] Between the two, the latter was more likely to form monodisperse NPs with fine particle size.^[18] However, TOP is very sensitive and is easily oxidized in air. It is critical to find a more easily handled phosphine as an alternative. Moreover, there have been few reports on Pd-P nanocatalysts for selective reactions.^[18] To the best of our knowledge, Pd-P NPs have not yet been investigated in the selective hydrogenation of alkynes. Herein, we reported the first fabrication of Pd-P NPs using inexpensive and stable triphenylphosphine (PPh₃) as phosphorous source. The monodisperse NPs were obtained with the smallest size ever reported (3.9 nm) and a novel single phase (Pd₃P_{0.95}). After annealing at 300 °C and 400 °C, the NPs grow to 4.0 and 4.8 nm, respectively. Notably, the well-crystallized 4.8 nm Pd-P NPs showed very high catalytic selectivity in semi- and stereoselective hydrogenation of alkynes. Without any additive, high selectivity of terminal alkene (e.g. styrene, 96%) and high Z/E ratio of internal alkene (e.g. ethyl cinnamate, 97:3) were obtained. With the help of quinoline, various terminal and internal alkenes were obtained in high yield (and Z/E selectivity). Notably, the deactivation of catalyst in this material by doping phosphorus was not observed at all in comparison with monometallic Pd/C.

The fabrication of colloidal Pd–P NPs was modified from our previous report.^[19] Briefly, palladium acetylacetonate (Pd(acac)₂, 0.1 mmol) and triphenylphosphine (TPP, 0.88 mmol) as Pd and P sources, trioctylphosphine oxide (TOPO, 1.16 g) as a surfactant, borane *tert*-butylamine complex (BTB, 1 mmol) as a reducing reagent, and oleylamine (OLA, 70%, 6.5 mL) as a co-reducing reagent as well as a stabilizer were used. A mixture of the above-mentioned chemicals was first deaerated at 50 °C using a nitrogen flow for 30 min, stirred at 220 °C for 30 min, and incubated at 270 °C for 15 min. A dark suspension finally formed, from which the colloidal Pd–P NPs were collected by centrifugation. The monodisperse NPs were then dispersed in hexane and characterized carefully. Transmission electron microscopy

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Supporting information for this article, including additional preparations details and characterizations of nanomaterials, is available on the WWW under http://dx.doi.org/10.1002/asia.201500939.



Figure 1. TEM image (A) and size distribution analysis (B) of OLA coated Pd– P NPs; TEM images, size distribution analysis, and XRD patterns of Pd–P/C after annealing at 300 °C (C, D, and G) or 400 °C (E, F, and H) for 1 h; Referenced XRD pattern of Pd₃P_{0.95} alloy with powder diffraction file (PDF) number #01-089-3046 (I).

(TEM, Figure 1 A) and size distribution analysis (Figure 1 B) showed the uniform NPs formed with an average size of 3.9 nm in diameter. In high resolution TEM (HRTEM, Figure S1 A in the Supporting Information), a lattice fringe of the NPs were measured as 0.235 nm, which is larger than that of the face-centered cubic Pd (111) plane (0.224 nm), indicating that the Pd–P alloy may have formed. Energy-dispersive X-ray spectros-copy (EDX) analysis further determined the coexistence of elemental Pd and P in one particle (Figure S1 B in the Supporting Information).

Next, the as-synthesized Pd–P NPs were deposited on activated carbon (Vulcan XC-72, Pd loading: 6.5 wt%) for catalysis use. Figure 1C, E show TEM images of the supported NPs after annealing at 300° C and 400° C under a nitrogen flow. Their

particle sizes increased to 4.0 nm and 4.8 nm (Figure 1 D, F), respectively, yet still with a narrow distribution each. When Figure 1 G (and Figure S2 A in the Supporting Information) is compared with Figure 1 H (and Figure S2 B in the Supporting Information), XRD patterns (and HRTEM images) indicated the crystalline structure of Pd–P NPs became much clearer. Both inductively coupled plasma mass spectrometry (ICP-MS, which determined the composition of Pd–P NPs as Pd₇₅P₂₅) and a reference XRD pattern (Figure 1 I) suggested a single phase in the annealed Pd–P NPs was Pd₃P_{0.95}. This is the first time this phase is reported in nanoparticles.

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The catalytic performance of the supported Pd–P NPs was evaluated in semi-hydrogenation reaction. The catalysts annealed at 300 °C and 400 °C are denoted Pd–P/C-300 and Pd–P/C-400, respectively. The reaction was performed using 0.13 mol% catalyst under one atmosphere of hydrogen gas in the presence of quinoline. As shown in Table 1, an impressive

Table 1. Optimization of the Conditions for Semi-Hydrogenation of Phenyl Acetylene.					
	La catalyst H ₂ 1a quinoli	(0.13 mol%) (1 atm) ine (1.1 eq)	/ _ 2a	+	
Entry	Catalyst	Solvent	Time	Selectivity 2a:3a ^[a]	
1 2 ^[b] 3 4 5 6 7 8 ^[c] 9 ^[c,d]	Pd/C Pd-P/C-300 Pd-P/C-400 Pd-P/C-400 Pd-P/C-400 Pd-P/C-400 Pd-P/C-400 Pd-P/C-400 Lindlar catalyst	EtOAc EtOAc EtOAc EtOAc (dehydrated) CH ₃ CN (dehydrated) MeOH/H₂O (25:1) MeOH/H ₂ O (25:1) MeOH/H ₂ O (25:1)	1.9 h 4.0 h 48 min 37 min 30 min 56 min 1.1 h 35 min 1.0 h	88:12 95:5 98:2 98:2 98:2 99:1 98:2 96:4 91:9	
Reaction conditions: 1a (0.5 mmol), solvent (5 mL), room temperature; the catalyst (0.13 mol%) was pretreated with additive quinoline (1.1 equiv) for 3 h. Conversion was >99% for alkynes in each case. [a] De- termined by GC-MS. [b] Reaction temperature was 50 °C. [c] In the ab- sence of quinoline. [d] 0.62 mol% of catalyst was used.					

selectivity for alkene was achieved using Pd–P/C-300 (entry 2) compared with commercial Pd/C (entry 1, TEM image shown in Figure S3 in the Supporting Information). To our surprise, when Pd–P/C-400 was used, both the activity and selectivity was further enhanced (entry 3). Dehydrated solvents accelerated the reaction but did not change the selectivity (entries 4 and 5). In entry 6, we found that a mixed solvent of MeOH and H₂O with a volume ratio of 25:1 was very special for the hydrogenation, and the alkene/alkane ratio reached up to 99:1. In entry 7, using larger amount of H₂O did not help. It is worth mentioning that a high selectivity for alkene (96%) was achieved even without additive (entry 8). In contrast, the traditional Lindlar catalyst (Pd-CaCO₃-PbO/PbAc₂) showed both low activity (0.62 mol% of Pd, 1.0 h) and low selectivity of 91% (entry 9).

Various terminal alkynes were investigated under the optimized conditions (Table 2). In entry 2, the bromide and in entries 3 and 4, other easily reduced groups were tolerated in

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Table 2. Semi-Hydrogenation of Terminal Alkynes.					
R-=== 1	Pd-P/C-400 (0.13 mo H ₂ (1 atm) quinoline (1.1 eq)	I%) ►	R+ 2	R3	
Entry	Alkyne		<i>t</i> [min]	Selectivity 2:3 ^[a]	
1		1a	56	99:1	
2	Br-	1 b	54	99:1	
3		1 c	24	99:1	
4	онс-	1 d	34	98:2	
5	C ₆ H ₁₃ ==	1 e	30	99:1	
6		1 f	24	95:5	
7	но	1 g	26	98:2	
8	Ph-	1 h	31	99:1 (96) ^[b]	
	2nd cycle		30	99:1	
	3rd cycle		36	99:1 (95) ^[b]	
	4th cycle		20	98:2	
	5th cycle		24	97:3 (95) ^[b]	
[a] Determined by GC-MS or ¹ H NMR. Conversion was $>$ 99% for alkynes. [b] Yield of isolated 2h shown in parenthesis.					

this transformation. The corresponding alkenes were obtained in higher than 98% yields. In entries 5 and 7, the hydrogenation of aliphatic alkyne and alcohol gave high selectivity for alkenes of 99% and 98%, respectively. In entry 6, diene can also be obtained in high selectivity of 95%. Finally in entry 8, the stability of the catalyst was investigated using 4-ethynylbiphenyl. After five cycles' test, the ratio of between alkene and alkane was remain as high as 97:3 with a 95% yield of isolated alkene. During the reuse process, the reaction time was not prolonged, which may indicate that active sites of catalyst were barely lost. Moreover, the selective semi-hydrogenation of several internal alkynes was also studied. As shown in Table 3, typical substrates including diphenylactylene (entry 1),

Table 3. Selective Semi-Hydrogenation of Internal Alkynes. ^[a]					
Entry	Alkyne	t	Alkene:Alkane	Z:E	
1 2 3 4 ^[b]	$\begin{array}{l} \mbox{Ph} \longrightarrow \mbox{Ph} & \mbox{Ph} &$	47 min 43 min 1.0 h 26 min	95:5 97:3 96:4 40:60	> 99:1 > 99:1 99:1 97:3	
The reactions were carried out under the above mentioned optimized conditions. Conversion was $>$ 99% for alkynes. [a] Selectivity was determined by ¹ H NMR spectroscopy. [b] Without quinoline.					

1-phenyl-1-propyne (entry 2), and ethyl phenylpropiolate (entry 3) were employed in the hydrogenation. The corresponding alkenes were obtained all in high yield of > 95%. Notably, besides the high double bond to single bond ratio, the excellent *Z:E* selectivity in alkenes were also achieved as above 99:1. In entry 4, high *Z:E* ratio of cinnamic acid was obtained

even in the absence of additive, although over-reduction of alkene was observed. The roles of quinoline may include two points: i) coordination to Pd to change the active sites of the catalyst; ii) reaction with hydrogen dissociated on Pd to decelerate the hydrogenation process.^[20] Therefore, the Pd–P/C-400 hybrid catalyst itself probably contributed to the stereospecific hydrogenation, while quinoline is important to suppress the total hydrogenation in the case of internal alkynes.

Considering that metal hydride formation is often the ratedetermined step for selective hydrogenation reactions, the doping of P was crucial for the excellent catalytic performance of Pd–P NPs. X-ray photoelectron spectroscopy (XPS) analysis determined a positive shift of Pd(3d) in Pd–P NPs compared to that in Pd/C (Figure 2 A). The binding energies of Pd(3d) in Pd/



Figure 2. XPS spectra on A) Pd(3d) and B) P(2p) of different Pd-based catalysts.

C, Pd–P/C-300, and Pd–P/C-400 increased gradually from 335.67 to 335.78 eV and 335.85 eV, respectively. Besides, the appearance of Pd-P-O peaks of P(2p) in both Pd–P/C-300 and Pd–P/C-400 (Figure 2B) also indicated the formation of Pd–P covalent bond and the electron flow from Pd to P, which suppressed the Pd hydride formation.^[11,12] Besides, P isolated the crystalline Pd atoms, which created a high barrier for the segregation of Pd atoms and their subsequent hydriding behavior.^[11,12] Additionally, P atoms could poison the surface by





blocking the most unsaturated sites, in the same way that lead was used to poison Pd.^[21] The hydrogenation would work through the Horiuti–Polanyi mechanism on moderately unsaturated Pd sites. The excellent *Z*-selectivity observed experimentally (Table 3) correlates well with this hypothesis.

In summary, we report the fabrication of monodisperse, ultrasmall, and single phase Pd–P NPs using PPh₃ as a phosphorus source for the first time. After a simple annealing process, the well-crystallized $Pd_3P_{0.95}$ NPs show excellent catalytic performance in chemoselective hydrogenation of alkynes. Various terminal and internal alkynes were investigated to produce corresponding alkenes in high chemoselectivity. The electronic deficiency of Pd in the Pd–P system probably contributed the high selectivity of the catalyst. It is the first time that Pd–P NPs have been used for selective semi-hydrogenation. The result is expected to promote the design of Pd–P or other metal-P nanocatalysts for various selective reactions.

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