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ARTICLE

Additive-Modulated Switchable Reaction Pathway in the Addition of Alkynes with Organosilanes Catalyzed by a Supported Pd Nanoparticles: Hydrosilylation versus Semihydrogenation

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Yanan Duan, ^{†a} Guijie Ji, ^{†a} Shaochun Zhang, ^{*}a Xiufang Chen ^a and Yong Yang ^{*a}

We herein report a supported Pd nanoparticles on N,O-doped hierarchical porous carbon as a single operation catalyst enabled additive-modulated reaction pathway for alkynes addition with organosilanes between hydrosilylation and semihydrogenation. In the case of alkynes hydrosilylation, a simple iodide ion as additive plays a promoted effect on activity, regio- and stereoselectivity, where iodide can coordinate with Pd NPs via strong δ donation to increase electron density of Pd atom, resulting in an increased ability for oxidative addition of hydrosilane as the rate-determining step to make the reaction proceed efficiently to afford vinylsilanes in high yields with excellent regio- and stereoselectivity. For catalytic transfer semihydrogenation of alkynes, water was introduced to mix with organosilane to form silanol together with generation of hydrogen atom on Pd NPs surface or liberation of H₂ gas as reducing agent, quantitative reduction of alkynes was achieved with exclusive selectivity to alkenes. In both cases, the catalyst can be recycled several times without significant loss in activity and selectivity. A broad range of alkyl and aryl alkynes with various functional groups is compatible with the reaction conditions. The role of the additive exerted in each reaction was extensively investigated through control experiments and kinetic isotopic effect along with spectroscopic characterization. In addition, the respective mechanism operated in both reactions was proposed.

Introduction

The importance of transformation reactions of alkynes in organic synthesis is undisputed, and various synthetic methodologies based on transition metal catalysis have been extensively developed for alkynes functionalization to produce a diverse array of chemicals in the past decade.¹ In this context, hydrosilylation and semihydrogenation of alkynes represent two significant and fundamental alkyne transformation reactions, enormous efforts have been dedicated in both industrial and academic community.

Transition-metal-catalyzed hydrosilylation of alkynes is the most straightforward and atom-economical approach to prepare synthetically valuable vinylsilanes, which are widely used as important synthetic intermediates in the fields of organic and medicinal chemistry, polymer chemistry as well as material science.² One key issue in the hydrosilylation of alkynes is the control of the regio- and stereochemistry because the reaction often results in the mixture of regio- and/or stereoisomers e.g., β -(E)-, β -(Z)-, and α -vinylsilane isomers operated via either *anti*-

Markovnikov or Markovnikov pathway that are usually difficult to separate. Worse still is that the regio- and stereoselectivity appears to be capriciously affected by various factors such as metal species, the ligand, the type of alkyne, and the silane, and the reaction parameters, such as solvent and temperature in most cases. Consequently, great efforts have been expended on the development of metal-catalyzed alkyne hydrosilylation with aim of regulating the reactions in a regio- and stereodefined fashion.

Until now, high-cost noble metal-compounds with Pt,³ Ru,⁴ Ir,⁵ Rh,⁶ and Pd⁷ have been most frequently used as catalysts for the hydrosilylation reaction. For example, platinum compounds such as Speier's⁸ and Karstedt's⁹ catalysts are the most widely employed industrial catalysts owing to their stability, high activity, and broad scope. Very recently, the late 3d transition metals – Fe,¹⁰ Co,¹¹ and Ni¹² – with their Earth-abundant, low-cost, and low-toxicity features have emerged as promising candidates for non-precious metal-based hydrosilylation catalysts. Despite such great achievements, the highly regio- and stereo-controlled hydrosilylation of alkynes still remains a grand challenge. On the other hand, the majority of those previously reported hydrosilylation reactions were prevailingly operated by homogenous metal-based complexes, which is a particularly significant drawback for their application in pharmaceutical and material industry because they are expensive, cannot be recycled, and difficult to separate from the product mixture. Furthermore, the current demand for green and sustainable transformation of organic molecules enhances the importance of heterogeneous catalysts that can facilitate the recycling of precious metals and helps to prevent contamination of

^a CAS Key Laboratory of Bio-Based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China. E-mail: zhangsc@qibebt.ac.cn; yangyong@qibebt.ac.cn

[†] These authors contributed equally.

Electronic Supplementary Information (ESI) available: Experimental and characterization details including Table S1-S3, Figure S1-S3, Scheme S1, kinetic isotope experiments and ¹H/¹³C NMR data for all β -(E)-vinylsilane compounds. See DOI: 10.1039/x0xx00000x

the products by toxic metals. In fact, there are only a few heterogeneous catalysts that have been exploited for alkyne hydrosilylation,^{3e,7b,7c,13} while a very recent work reported by Cai^{7e} catalysed by bimetallic Pd-Cu nanoparticles supported on SiO₂ showed high activity and regio- and stereoselectivity, but generally still suffer from low catalytic efficiency, poor regio- and stereoselectivity, and limited substrate scope. Therefore, it is highly desirable to develop a novel recyclable heterogeneous catalyst that can effectively catalyze hydrosilylation of a wide range of functionalized alkynes with remarkable regio- and stereoselectivity under ambient conditions.

Most recently, we developed a highly efficient and recyclable supported Pd nanoparticles (NPs) on N,O-dual doped hierarchical porous carbon (Pd@N,O-Carbon) derived from naturally renewable biomass - bamboo shoots for catalytic semihydrogenation of alkynes.¹⁴ To further explore its applications in other organic transformations, we herein report our recent results regarding additive-modulated switchable reaction pathway in the addition of alkynes with organosilanes to proceed via either hydrosilylation or transfer semihydrogenation pathway to efficiently and chemoselectively afford their corresponding vinylsilanes and alkenes, respectively, under mild reaction conditions.

Results and discussion

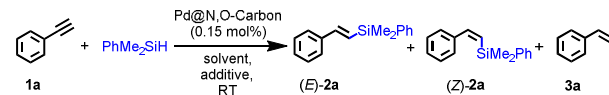
Preparation of Pd@N,O-Carbon. The preparation and characterization details of the supported Pd NPs catalyst Pd@N,O-Carbon were reported in our recent paper.¹⁴ Briefly, the novel N,O-dual-doped porous carbon material with large specific surface area (up to 1037 m²g⁻¹) and high nitrogen content (3.32 wt%) was synthesized from naturally renewable fresh bamboo shoots by a facile tandem hydrothermal-carbonization processes in a simple, direct and environmentally-benign manner without using any templates or chemical agents for activation. The catalyst Pd@N,O-Carbon was prepared by a typical wet chemical impregnation and reduction method using hydrazine hydrate with average Pd particle size of 11.9 nm and loading of 1.64 wt%.

Hydrosilylation of Alkynes. We commenced our study by examining Pd@N,O-Carbon as the catalyst for hydrosilylation of phenylacetylene (**1a**) with PhMe₂SiH as a benchmark reaction to optimize the reaction conditions, and selected results are compiled in Table 1. The reaction was first carried out with 0.15 mol% (5 mg) of Pd@N,O-Carbon in anhydrous THF at room temperature. The reaction proceeded sluggishly, with 10% conversion of **1a** into styrene (**3a**) as sole product without any formation of vinylsilanes (**2a**) after overnight (entry 1). To our great delight, in the presence of 1 or

even 0.1 equivalent of an iodide salt TBAI, full conversion was accomplished within 120 min, affording a mixture of anti-Markovnikov ((*E* + *Z*)-**2a**) products with the (*E*)-isomer as the main product (entries 2-5). Particularly, excellent regio- and stereoselectivity to vinylsilane with *E/Z* ratio of being 96/2 was achieved when 0.5 equivalent of TBAI was employed. Of note, the iodide concentration [*I*⁻] has a significant effect on the reaction rate albeit with almost negligible change in regio- and stereoselectivity to vinylsilane (*E/Z* ratio ranging from 89:3 to 96:2), in which the reaction rates were dramatically enhanced with an increase of [*I*⁻] (Figure S1 in the Supporting Information). In sharp contrast, the

analogous bromide salt TBAB is much less effective (entry 6) and the chloride TBAC is ineffective for the transformation (entry 7). Other NaI or NH₄I was equally effective for the reaction with slight decrease in regio-

Table 1. Condition Optimization for Alkyne Hydrosilylation^a



| Entry | Solvent | Additive (equiv) | Time (min) | Conversion (%) ^b | Selectivity (%) ^c | | |
|-----------------|---------------------------------|-------------------------|------------|-----------------------------|------------------------------|-------------------------|-----------|
| | | | | | (<i>E</i>)- 2a | (<i>Z</i>)- 2a | 3a |
| 1 | THF | none | 720 | 10 | - | - | 100 |
| 2 | THF | TBAI (1.0) | 50 | 100 | 89 | 3 | 8 |
| 3 | THF | TBAI (0.5) | 120 | 100 | 96 | 2 | 2 |
| 4 | THF | TBAI (0.25) | 120 | 100 | 94 | 2 | 4 |
| 5 | THF | TBAI (0.1) | 120 | 100 | 93 | 6 | 1 |
| 6 | THF | TBAB (0.5) | 120 | 10 | 82 | 9 | 9 |
| 7 | THF | TBAC (0.5) | 120 | 2 | - | - | 100 |
| 8 | THF | NaI (1.0) | 70 | 100 | 84 | 10 | 6 |
| 9 | THF | NH ₄ I (1.0) | 70 | 100 | 86 | 7 | 7 |
| 10 | THF | I ₂ (0.5) | 1200 | 16 | 79 | 10 | 11 |
| 11 ^d | THF | TBAI (0.5) | 1440 | 100 | 92 | 2 | 6 |
| 12 ^e | THF | TBAI (0.5) | 300 | 4 | - | - | 100 |
| 13 ^f | THF | none | 1440 | 0 | - | - | - |
| 14 ^g | THF | TBAI (0.5) | 200 | 100 | 92 | 2 | 4 |
| 15 | CH ₃ CN | TBAI (0.5) | 120 | 38 | 91 | 0 | 9 |
| 16 | CH ₂ Cl ₂ | TBAI (0.5) | 120 | 74 | 86 | 6 | 8 |
| 17 | DMSO | TBAI (0.5) | 120 | 32 | 88 | 4 | 8 |
| 18 | DMF | TBAI (0.5) | 120 | 44 | 88 | 3 | 9 |
| 19 | Toluene | TBAI (0.5) | 120 | 0 | - | - | - |

^aReaction conditions: **1a** (0.5 mmol), PhMe₂SiH (0.6 mmol), Pd@N,O-Carbon (5 mg, 0.15 mol% of Pd), solvent (1 mL), room temperature. ^bdetermined by GC-FID using dodecane as the internal standard. ^cdetermined by ¹H NMR spectroscopy. ^dPd@N,O-Carbon (1 mg, 0.03 mol% of Pd). ^eWithout using Pd@N,O-Carbon. ^fWithout using Pd@N,O-Carbon and *I*⁻ source. ^gActivated carbon as support.

and stereoselectivity (entries 8 and 9). However, the reaction proceeded poorly in the presence of I₂ under otherwise identical conditions (entry 10). Those results thereby clearly indicate that it is the iodide ion that promotes the catalysis, resulting in a significantly increased reaction efficiency. Remarkably, the catalyst loading could be decreased to 0.03 mol% without any influence on chemical yield and the regio- and stereoselectivity to **2a** albeit with a longer reaction times, in which the TON is as high as 1,667 (entry 11). In addition, the reaction nearly shut down in the absence of either Pd@N,O-Carbon, or simple iodide ion, or both (entries 1, 12 and 13), indicating that the reaction was enabled by the combination of Pd@N,O-Carbon and *I*⁻ anion in concert. For comparison, the supported catalyst adopting commonly used activated carbon with larger surface area (1580 m²/g) without N-doping as support showed inferior activity and relatively lower regio- and stereoselectivity under otherwise identical conditions (entry 14). Subsequently, several different solvents were involved to investigate the influence on the hydrosilylation reaction (entries 15-19). Among the solvents employed, THF was found to be the best choice for the formation of (*E*)-anti-Markovnikov vinylsilane product.

Have identified the optimal reaction conditions, we next investigated the substrate scope to explore the versatility of this hydrosilylation protocol (Table 2). In general, the catalyst Pd@N,O-Carbon enabled the hydrosilylation of a diverse array of terminal

alkynes with PhMe_2SiH , providing the corresponding vinylsilanes in high yields with excellent regio- and stereoselectivity. Aryl alkynes bearing either electron-donating or electron-withdrawing groups were effectively hydrosilylated, and substituents in the *para*-, *meta*-, and *ortho*- positions of the aryl ring are compatible with the reaction

conditions. However, substrates with *ortho*- substituents (**1b** and **1e**)

Table 2. Substrate Scope of Alkynes^a

| $\text{R}^1\text{—C}\equiv\text{C—R}^2 + \text{PhMe}_2\text{SiH} \xrightarrow[\text{THF, TBAI, RT}]{\text{Pd@N,O-Carbon (0.15 mol\%)}} \text{R}^1\text{—CH=CH—SiMe}_2\text{Ph} + \text{R}^2\text{—CH=CH—SiMe}_2\text{Ph}$ | | | | | |
|---|---------|----------|-----------------------------|------------------------|----------------------|
| 1a-r | | | | (E)-2a-r | (Z)-2a-r |
| Entry | Product | time (h) | Conversion (%) ^b | Yield (%) ^c | E/Z (%) ^d |
| 1 | | 2 | >99 | 96 | 98/2 |
| 2 | | 4 | >99 | 95 | 88/12 |
| 3 | | 2 | >99 | 97 | 94/6 |
| 4 | | 2 | >99 | 96 | 94/6 |
| 5 | | 6 | >99 | 98 | 51/49 |
| 6 | | 4 | >99 | 98 | 92/8 |
| 7 | | 2 | >99 | 60 | 93/7 |
| 8 | | 2 | >99 | 96 | 96/4 |
| 9 | | 2 | >99 | 91 | 98/2 |
| 10 | | 24 | >99 | 92 | 94/6 |
| 11 | | 2 | >99 | 93 | 92/8 |
| 12 | | 24 | 8 | 6 | >99/1 |
| 13 | | 16 | >99 | 85 | 91/9 |
| 14 | | 9 | >99 | 97 | >99/1 |
| 15 | | 2 | >99 | 97 | >99/1 |
| 16 | | 20 | >99 | 96 | >99/1 |
| 17 | | 4 | >99 | 98 | >99/1 ^e |
| 18 | | 18 | >99 | 98 | >99/1 ^e |

^aReaction conditions: **1a-r** (0.5 mmol), PhMe_2SiH (0.6 mmol), TBAI (0.25 mmol), Pd@N,O-Carbon (5 mg, 0.15 mol% of Pd), THF (1 mL), room temperature under Ar atmosphere.

^bdetermined by GC-FID using dodecane as the internal standard. ^cisolated yield of product.

^ddetermined by ¹H NMR spectroscopy. ^e*trans*-/*cis*-configuration ratio according to ¹H NMR spectroscopy.

appeared to be less reactive than their *para*- or *meta*-substituted analogues where relatively longer times were required for full conversion, possibly due to the steric effect. Halogen-substituted aryl alkynes (**1h** and **1i**) underwent anti-Markovnikov hydrosilylation in high yields with excellent regio- and stereoselectivity, and dehalogenation products were not observed. Amine (**1j**) and hydroxyl (**1k**) functional groups were also tolerated with the present conditions. Heteroaromatic alkyne, 2-ethynylthiophene (**1m**), proceeded smoothly to deliver the corresponding vinylsilane products (**2m**) in high yield with excellent regio- and stereoselectivity. However, 3-ethynylpyridine (**1l**) was almost ineffective and gave poor activity. It is worthy to point out that those substrates featuring functional groups (**1j**, **1l**, and **1m**,

e.g. NH_2 -, pyridine-, and thiophene-) with potential to coordinate or interact with Pd NPs required considerably longer reaction times for complete conversion. Not only terminal aryl alkynes but also terminal alkyl alkynes (**1n-p**) are also suitable substrates and underwent the hydrosilylation reaction under the optimized conditions to afford the product in high yields. Surprisingly, in these cases, exclusive regio- and stereoselectivity to (*E*)-isomer vinylsilanes were achieved under otherwise identical conditions, which is the first example with perfect regio- and

Table 3. Substrate Scope of Hydrosilanes^a

| $\text{Ph—C}\equiv\text{C—H} + \text{H—Si} \xrightarrow[\text{THF, TBAI, RT}]{\text{Pd@N,O-Carbon (0.15 mol\%)}} \text{Ph—CH=CH—Si} + \text{Ph—CH=CH—Si}$ | | | | | |
|---|-----------------------------|----------|-----------------------------|------------------------|----------------------|
| Ph—C≡C—H | | | | (E) | (Z) |
| Entry | H-Si | time (h) | Conversion (%) ^b | Yield (%) ^c | E/Z (%) ^d |
| 1 | PhMe_2SiH | 2 | >99 | 96 | 98/2 |
| 2 | Et_3SiH | 6 | >99 | 93 | 89/11 |
| 3 | $(n\text{-Bu})_3\text{SiH}$ | 24 | 72 | 71 | 87/13 |
| 4 | $(\text{EtO})_3\text{SiH}$ | 24 | nr ^e | - | - |
| 5 | $(i\text{-Pr})_3\text{SiH}$ | 24 | nr ^e | - | - |
| 6 | Ph_3SiH | 24 | nr ^e | - | - |
| 7 | Ph_2SiH_2 | 24 | >99 | 89 | >99/1 |
| 8 | PhSiH_3 | 24 | nr ^e | - | - |

^aReaction conditions: phenylacetylene (0.5 mmol), hydrosilane (0.6 mmol), TBAI (0.25 mmol), Pd@N,O-Carbon (5 mg, 0.15 mol% of Pd), THF (1 mL), room temperature under Ar atmosphere. ^bdetermined by GC-FID using dodecane as the internal standard. ^cisolated yield of product. ^ddetermined by ¹H NMR spectroscopy. ^eno reaction.

stereoselective hydrosilylation of terminal alkynes thus far to our knowledge. Particularly, nitrile and hydroxyl moieties in the alkyl chains (**1o** and **1p**) were compatible with the reaction conditions as well. In addition, the reaction of internal aryl and alkyl alkynes (either symmetric or unsymmetric), such as diphenylacetylene (**1q**) and ethyl 2-butyrate (**1r**), exclusively provided the *syn* addition products **2q** and **2r** in high yields with perfect *trans* configurations, respectively. Notably, no formation of Markovnikov *gem*-vinylsilane products was observed in all cases listed in Table 2.

Subsequently, we further explore the compatibility of various hydrosilanes for alkyne hydrosilylation reaction. A diverse range of hydrosilanes including primary-, secondary-, and tertiary- was employed, and the results are summarized in Table 3. Overall, the reactions are highly dependent on hydrosilane- substrates in terms of activity and regio- and stereoselectivity. Tertiary hydrosilanes, which are much more commercially relevant and are widely used to make silicones and silane coupling reagents, are preferentially favorable to the hydrosilylation in this catalytic system, but the steric hindrance of substituents on silicon exhibited a significant influence on reaction efficiency. For example, PhMe_2SiH was very active, giving the corresponding vinylsilane in 96% yield with excellent regio- and stereoselectivity, whereas with the use of triethylsilane, tributylsilane, and triisopropylsilane, and triethoxysilane, respectively, the yields to the corresponding vinylsilanes was decreased dramatically accompanied with slight decline in regio- and stereoselectivity; particularly, the steric demanding triisopropylsilane, triethoxysilane, and triphenylsilane completely shut down the reaction (entries 4-6). Secondary

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hydrosilanes, e.g., diphenylsilane, are also compatible with the reaction conditions, affording the desired vinylsilane in high yield with perfect stereoselectivity albeit with considerably longer reaction times (entry 7). Unfortunately, primary hydrosilanes, e.g., phenylsilane failed to the hydrosilylation under otherwise identical conditions (entry 8).

To verify whether the observed catalysis was due to the heterogeneous catalyst Pd@N,O-Carbon or a leached Pd species in solution, we carried out the addition of phenylacetylene (**1a**) with PhMe₂SiH and removed the catalyst from the reaction mixture by filtration at approximately 50% conversion of **1a**. After removal of the Pd@N,O-Carbon, the filtrate was again held at room temperature for continuing reaction. In this case, no significant increase in conversion was observed, indicating that leached Pd species from the catalyst (if any) are not responsible for the observed activity (Figure 1 (B)). It was confirmed by ICP-AES analysis that no Pd species could be detected in the filtrate (below the detection limit). The catalyst Pd@N,O-Carbon could be recovered by centrifuged and reused at least 6 times for the transformation of **1a** and PhMe₂SiH without any significant loss of catalytic activity and regioselectivity, as shown in Figure 1 (A). Taken together, these results rule out any contribution to the observed catalysis from a homogeneous Pd species, demonstrating that the observed catalysis was intrinsically heterogeneous.

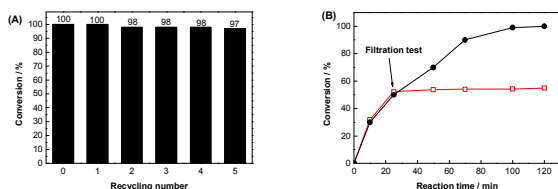




Figure 1. Stability of the catalyst Pd@N,O-Carbon for phenylacetylene hydrosilylation with PhMe₂SiH under standard conditions.

Catalytic Transfer Semihydrogenation of Alkynes. Metal-catalyzed alkyne semihydrogenation is a key industrial reaction to manufacture polymer-grade alkenes and to access new chemicals, pharmaceuticals, and some natural products with stereodefined alkene functionalities.^{15,16} To date, the chemoselective semihydrogenation of alkynes still remains a great challenge mainly due to the easy overreduction of alkenes to undesired alkanes. In general, Pd-based catalysts were most widely used catalysts for the semihydrogenation transformation using hydrogen gas as reductant. Especially, the Lindlar catalyst¹⁷ (Pd/CaCO₃ treated with Pb salts and quinoline) is still the best choice for the industrial settings, while the use of toxic lead or a large amount of quinoline together with flammable H₂ gas as reductant is an environmental and safety issue. In contrast, catalytic transfer semihydrogenation using various hydrogen donors as reducing agents complements to catalytic semihydrogenation, which has apparent advantages, including safer operation and better control of chemoselectivity of alkenes. As a consequence, a number of metal-based transfer semihydrogenation of alkynes have been developed with aim of obviating the need for hydrogen gas and toxic additives.¹⁸ Among them, a mixture of hydrosilanes with either water or alcohols being one of the reducing agents has been employed for Cu,¹⁹ Au²⁰ or

Pd^{7b}-catalyzed transfer semihydrogenation of alkynes. However, a recyclable and efficient heterogeneous catalyst enabled such transformation with outstanding chemoselectivity and broad substrate scopes with excellent compatibility of functional groups is still relatively rare thus far.

Bearing in mind that alkynes are able to be semireduced into alkenes mediated by metal-based catalysts in the presence of hydrosilanes and water or alcohols, we envisioned whether the catalytic transfer semihydrogenation of alkynes could be realized

Table 4. Condition Optimization for Catalytic Transfer Semihydrogenation^a

| | | | | | |
|---|----------------------------------|---------------------------------|------------|---|--------------------------------------|
| | | Pd/N,O-Carbon (0.15 mol%) | | overreduction | |
|  | | hydrosilane/H ₂ O | |  | |
| 1a | | Solvent, 70°C | | 4a | |
| Entry | Silane | Solvent | Time (min) | Conversion (%) ^b | Selectivity (3a/4a) (%) ^b |
| 1 | PhMe ₂ SiH | DMSO | 20 | 100 | >99/1 |
| 2 | PhMe ₂ SiH | CH ₂ Cl ₂ | 120 | 5 | >99/1 |
| 3 | PhMe ₂ SiH | Toluene | 90 | 4 | >99/1 |
| 4 | PhMe ₂ SiH | CH ₃ CN | 90 | 54 | 91/9 |
| 5 | PhMe ₂ SiH | DMF | 50 | 100 | 98/2 |
| 6 | PhMe ₂ SiH | THF | 90 | 29 | 99/1 |
| 7 | PhMe ₂ SiH | H ₂ O | 180 | 2 | >99/1 |
| 8 | PhMe ₂ SiH | EtOH | 360 | 3 | >99/1 |
| 9 | Ph ₃ SiH | DMSO | 180 | 10 | >99/1 |
| 10 | Ph ₂ SiH ₂ | DMSO | 90 | 100 | 98/2 |
| 11 | PhSiH ₃ | DMSO | 240 | 100 | 98/2 |
| 12 | Et ₃ SiH | DMSO | 900 | 100 | >99/1 |
| 13 | Bu ₃ SiH | DMSO | 1080 | 95 | 90/10 |
| 14 | PMHS | DMSO | 600 | 100 | 93/7 |
| 15 ^c | PhMe ₂ SiH | DMSO | 60 | 100 | >99/1 |
| 16 ^d | PhMe ₂ SiH | DMSO | 720 | 0 | - |
| 17 ^e | none | DMSO | 720 | 0 | - |
| 18 ^f | PhMe ₂ SiH | DMSO | 720 | 0 | - |
| 19 ^g | PhMe ₂ SiH | DMSO | 20 | 100 | >99/1 |
| 20 ^h | PhMe ₂ SiH | DMSO | 20 | 100 | >99/1 |

























^aReaction conditions: **1a** (0.5 mmol), hydrosilane (0.75 mmol), H₂O (1.0 mmol), Pd@N,O-Carbon (5 mg, 0.15 mol% of Pd), solvent (1 mL), 70°C under Ar atmosphere. ^bDetermined by GC-FID using dodecane as the internal standard. ^c1 mg (0.03 mol% of Pd) Pd@N,O-Carbon. ^dWithout using Pd@N,O-Carbon. ^eWithout using hydrosilane. ^fWithout using H₂O. ^gMethanol (1.0 mmol) instead of H₂O. ^hEthanol (1.0 mmol) instead of H₂O.

in the presence of Pd@N,O-Carbon. We chose phenylacetylene (**1a**) as a model substrate to assess the catalytic efficiency, the results are listed in Table 4. **1a** was first treated with the mixture of PhMe₂SiH and H₂O as reducing agent in DMSO at 70°C. We are pleased to observe that the reaction proceeded efficiently to produce the target styrene (**3a**) exclusively in quantitative yield within 20 min without any formation of undesired ethylbenzene (**4a**) even after full conversion of **1a** was achieved (entry 1), which hardly could be achieved in the catalytic semihydrogenation with H₂.¹⁵

Encouraged by this finding, a set of factors was subsequently investigated to examine the reaction efficiency. Firstly, the reaction was performed in various organic solvents, including THF, CH₂Cl₂, toluene, CH₃CN, DMF, respectively (entries 2-6). Under otherwise

identical reaction conditions, DMSO was found to be the best choice to give superior catalytic performance in terms of both activity and chemoselectivity among the solvents employed. However, poor activity was observed when the reaction was subjected to the pure H₂O or ethanol as solvent (entries 7 and 8). Subsequently, the reaction was conducted at varying temperatures. An increase of reaction temperature (from room temperature to 70°C) considerably enhances the reaction rate without affecting the chemoselectivity to styrene, whereas further elevating reaction temperature to 80°C resulted in a drastic decrease of chemoselectivity to styrene albeit with ever faster reaction rate (Table S1 in the Supporting

Table 5. Substrate Scopes for Catalytic Transfer Semihydrogenation^a

| $\text{R}-\text{C}\equiv\text{C}-\text{H} \xrightarrow[\text{1 mL DMSO, 70}^\circ\text{C}]{\text{Pd@N,O-Carbon (0.15 mol\% of Pd), PhMe}_2\text{SiH/H}_2\text{O (0.75/1)}} \text{R}-\text{C}=\text{C}-\text{H}$ | | | | |
|---|--|---------------------|-----------------------------|------------------------------|
| Entry | Product | Reaction time (min) | Conversion (%) ^b | Selectivity (%) ^b |
| 1 |  (3a) | 20 | >99 | >99 |
| 2 |  (3b) | 30 | >99 | >99 |
| 3 |  (3c) | 30 | >99 | >99 |
| 4 |  (3d) | 30 | >99 | >99 |
| 5 |  (3e) | 30 | >99 | >99 |
| 6 |  (3f) | 30 | >99 | >99 |
| 7 |  (3g) | 60 | >99 | >99 |
| 8 |  (3h) | 60 | >99 | >99 |
| 9 |  (3i) | 30 | >99 | >99 |
| 10 |  (3j) | 50 | >99 | >99 |
| 11 |  (3k) | 80 | >99 | >99 |
| 12 |  (3l) | 120 | >99 | >99 |
| 13 |  (3m) | 30 | >99 | >99 |
| 14 |  (3n) | 60 | >99 | >99 |
| 15 |  (3o) | 24(h) | trace | - |
| 16 |  (3p) | 60 | >99 | >99 |
| 17 |  (3q) | 20 | >99 | >99 |
| 18 |  (3r) | 25 | >99 | >99 |
| 19 |  (3s) | 25 | >99 | >99 |
| 20 |  (3t) | 90 | >99 | >99 |
| 21 |  (3u) | 360 | 70 | >99 |
| 22 |  (3v) | 30 | >99 | >99 |
| 23 ^c |  (3w) | 24(h) | 75 | >99 (96/4) ^d |
| 24 ^c |  (3x) | 24(h) | 95 | >99 (96/4) ^d |

^aReaction conditions: **1a-t** (0.5 mmol), PhMe₂SiH (0.75 mmol), H₂O (1.0 mmol), Pd@N,O-Carbon (5 mg, 0.15 mol% of Pd), DMSO (1 mL), 70°C under Ar atmosphere. ^bdetermined by GC-FID using dodecane as the internal standard. ^cPd@N,O-Carbon (15 mg, 0.45 mol% of Pd). ^dratio of E/Z-isomer determined by ¹H NMR spectroscopy.

Information). Next, a spectrum of hydrosilanes was further applied in combination with H₂O as reducing agent for the semihydrogenation reaction. It turned out that the steric hindrance of substituents on silicon exhibited a significant influence on reaction efficiency. For example, diphenylsilane is still active, giving **3a** in 100% conversion with 98% selectivity (entry 10), while with the use of triphenylsilane, the reaction rate was decreased dramatically (entry 9). Other alkyl substituted tertiary silanes, e.g., triethylsilane and tributylsilane, worked as well for the semihydrogenation, but the reaction rates are extremely slower

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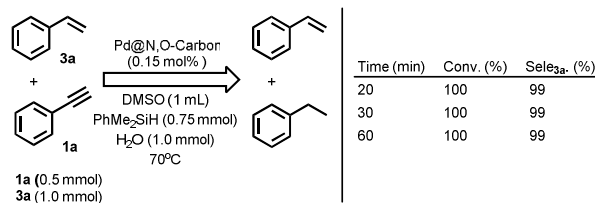
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than that of PhMe₂SiH under other identical conditions (entries 12 and 13). Notably, PMHS (poly(methylhydrosiloxane)), an abundant, nontoxic, moisture-stable, and inexpensive by-product of the silicone industry, is also applicable to the reaction with slightly lower chemoselectivity to styrene and a bit longer reaction times (entry 14).

Furthermore, the concentration of hydrosilane significantly influences both reaction rate and chemoselectivity (Table S2 in the Supporting Information). An increase of PhMe₂SiH concentration considerably shortens the reaction time for full conversion, but higher concentrations caused partial overhydrogenation to undesired alkane. Likewise, the amount of H₂O involved also affects the reaction rates but without influencing the chemoselectivity to styrene. The more amount of H₂O was added, the faster the reaction proceeded but levelled off at higher concentrations (Table S3 in the Supporting Information). Lastly, the control experiments showed that the catalyst loading could be lowered to 1 mg (0.03 mol% of Pd) in which full conversion was achieved within 60 min with delivery of styrene as sole product (entry 15). However, no reaction proceeded at all in the absence of either catalyst, or hydrosilane, or water under identical conditions, indicating that the combination of three components is indispensable for the success of semihydrogenation (entries 16–18). Worthy to notice that alcohols, such as MeOH and EtOH, can be used instead of H₂O that is also capable of catalyzing the semihydrogenation with comparable catalytic efficiency (entries 19 and 20).

With the optimized reaction conditions in hand, we next investigated the substrate scope to explore the versatility of the present protocol, the results are compiled in Table 5. Overall, the reactions proceeded in nearly quantitative yields (>99%) with exclusive selectivity to the desired alkenes for a diverse array of alkynes under the standard conditions. Electron-donating and electron-withdrawing substituents at the *meta*-, *ortho*-, *para*-positions on the phenyl ring of aromatic alkynes all gave high yields to their corresponding alkenes (entries 1–10). Gratifyingly, phenylacetylenes bearing amine, hydroxyl, cyano, chloro, fluoro, bromo, or ester, aldehyde substituents were all tolerated by this protocol, giving the corresponding styrenes in >99% yields (entries 5–14). The sulfur-containing alkyne, 2-ethynylthiophene (**1p**), was hydrogenated in full conversion with perfect selectivity (entry 14), while the presence of pyridine moiety in the alkyne (**1o**), the reaction shut down without observation any product even prolonging the reaction time to 24 h under otherwise identical conditions (entry 15), indicative of the strong interaction between substrate and Pd NPs. Not only terminal aryl alkynes, but terminal aliphatic alkynes even those containing functional groups, such as hydroxyl, cyano, ester, or carboxylic acid could also be efficiently reduced into the corresponding alkenes in high yields with perfect selectivity (entries 17–22). In addition, the unsymmetric internal alkynes (entries 23 and 24) are also able to be semihydrogenated to their corresponding alkene in moderate to high yield with excellent *E/Z* ratio while longer reaction times are required.

More importantly, the catalyst Pd@N,O-Carbon demonstrated excellent chemoselectivity for alkynes over alkenes (Scheme 1). For example, a mixture of styrene and phenylacetylene with an excess of styrene was subjected to the present catalysis conditions,



Scheme 1. Demonstration of highly chemoselective alkyne semihydrogenation catalyzed by Pd@N,O-Carbon.

phenylacetylene was semihydrogenated completely and styrene was obtained in 99% purity even prolonging the reaction times after full consumption of phenylacetylene. Similarly, when styrene was subjected to this catalysis conditions, almost no formation of ethylbenzene was observed (Scheme S1 in the Supporting Information). These results highlight the potential application for the industrial purification of alkenes.

The catalyst Pd@N,O-Carbon also showed robust stability for the catalytic transfer semihydrogenation. After the reaction, the solid catalyst was recovered by centrifugation, washed with ethanol thoroughly, dried under vacuum and reused under the standard conditions. The Pd@N,O-Carbon catalyst could be recycled up to 6 times without significant loss in catalytic activity (Figure 2 (A)). Hot filtration experiment further verifies that the heterogeneity of the catalyst. The reaction was stopped when the conversion was approaching approximately 65%, the solid catalyst was filtered and the filtrate was again hold under standard conditions for continuous reaction. In this case, no increase in conversion was observed (Figure 2 (B)). The ICP-AES analysis of the filtrate showed no leaching of Pd species in the solution. Taken together, all results strongly indicate that the intrinsic role of the heterogeneous Pd@N,O-Carbon in catalysis.

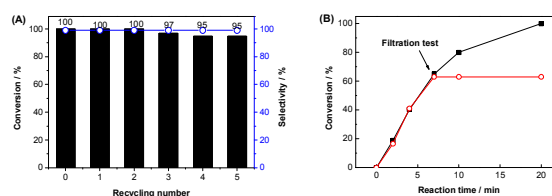


Figure 2. Stability of the catalyst Pd@N,O-Carbon for phenylacetylene transfer semihydrogenation under standard conditions.

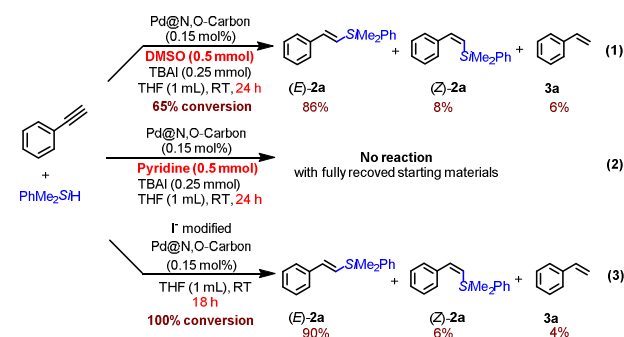
Mechanism Studies for Alkyne Hydrosilylation and Transfer Semihydrogenation. Two mechanisms of metal-catalyzed hydrosilylation of alkynes have been arguably but widely accepted, the classic Chalk-Harrod²¹ and the modified Chalk-Harrod mechanisms²². In either case, mechanism starts with an oxidative addition of hydrosilane to the metal, followed by sequential coordination and hydrometalation of the alkyne. In the Chalk-Harrod mechanism, the insertion of alkyne into the M-H bond takes place first, while for the second mechanism, M-Si insertion occurs first. Subsequently, the catalytic cycle followed by reductive elimination to give the *syn*- or *trans*-addition product β -(*E* or *Z*)-vinylsilane, which is highly dependent on the catalyst and/or substrate as well as other factors such as type of ligands and

solvents. Without doubt, the oxidative addition step generally recognized as the rate-determining step plays a decisive role on the overall catalytic activity and regio- and stereoselectivity for alkyne hydrosilylation. On the other hand, while iodides have been employed to promote Pd-catalyzed alkyne hydrosilylation,^{7c, 7e} the intrinsically detailed roles of I⁻ ion exerted in the transformation have not been elucidated thus far.

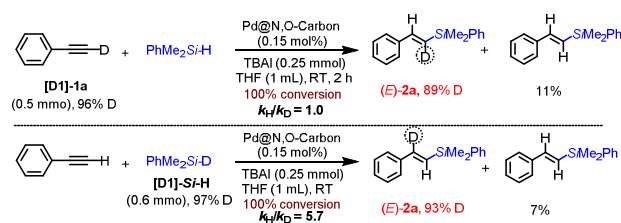
To understand the plausible reaction pathway of this heterogeneous Pd NPs catalyzed regio- and stereoselective hydrosilylation of alkynes promoted by a simple I⁻ ion, additional experiments were extensively performed. Firstly, to probe the essential role of TBAI as additive which exerted a pronounced effect in the present alkyne hydrosilylation, the catalyst Pd@N,O-Carbon was treated with DMSO as a 'poisoning' agent for 20 mins to interact with Pd NPs before introduction of phenylacetylene **1a**, PhMe₂SiH and TBAI in THF under otherwise identical reaction conditions. DMSO

has been reported to be a suitable ligand to cap Pd NPs without affecting the capability to coordinate with alkynes.²³ In this case, a drastic decrease in reaction rate was observed and only 65% of **1a** was converted after 24 h, affording vinylsilane with satisfactory regio- and stereoselectivity (Scheme 2-(1)). In contrast, when pyridine was used as a poisoning agent instead, which has much stronger coordination ability than DMSO, no conversion of **1a** to the desired vinylsilane was observed with fully recovered starting materials (Scheme 2-(2)). Such results indicate that the in-situ generated Pd NPs coordinated by I⁻ are catalytically active species for alkyne hydrosilylation to a great extent.

To confirm this, we prepared the iodide modified catalyst Pd@N,O-Carbon, in which the catalyst Pd@N,O-Carbon was treated with TBAI in THF followed by filter and washing with methanol thoroughly to remove any remaining free I⁻ ion on the support. XPS characterization of the modified catalyst shows that the peaks of I⁻ at 619.2 and 630.7 eV, assignable to 3d_{5/2} and 3d_{3/2} were observed (Figure S2 in the Supporting Information). Meanwhile, the binding energy (BE) value of Pd 3d_{5/2} slightly shifted to the higher BE as compared with the unmodified Pd@N,O-Carbon, indicating that the strong interaction between I⁻ and Pd NPs surface. More interestingly, the iodide modified catalyst Pd@N,O-Carbon exhibited high catalytic activity for hydrosilylation with excellent regio- and stereoselectivity to vinylsilane, while a considerably longer reaction times is required (Scheme 2-(3)). However, such results can't be achieved in the only presence of Pd@N,O-Carbon under otherwise identical reaction conditions as mentioned in Table 1, entry 1.



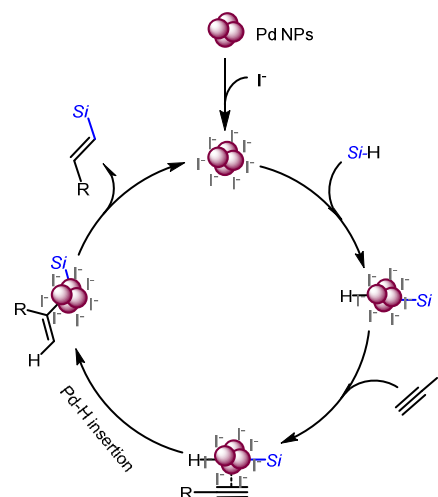
Scheme 2. Role of iodide for alkyne hydrosilylation.



Scheme 3. Deuterium labeling experiments and kinetic isotopic effect studies.

Bearing in mind that the unusual effects of iodide in catalysis which have been well-documented,²⁴ these results suggest that in the presence of I⁻, catalytically active Pd(0)I_n species were formed through strong δ interaction between the soft iodide and Pd NPs. On the other hand, the I⁻ as an ancillary ligand has the strong ability to donate electron density to metallic Pd(0), which is preferentially favorable for the oxidative addition of hydrosilane, resulting in the increased catalytic efficiency. This is also in good agreement with the observation reported by Pleixats and co-authors,^{7b} whereas Pd NPs was stabilized by tri-imidazolium tetrafluoroborates. Of note, in their case, high catalyst loading, larger excess of hydrosilane, elevated temperature and longer reaction times as well were necessary to ensure the success for alkyne hydrosilylation.

Subsequently, the deuterium labeling experiments were carried out (see Supporting Information for details). A relatively larger KIE ($k_H/k_D = 5.7$, Scheme 3) was observed for the addition of **1a** with [D1]-PhMe₂SiH with 93% D-incorporation in the vinylsilane, and this indicates that cleavage of the Si-H bond of the hydrosilane takes place in the course of reaction as a result of the oxidative addition of PhMe₂SiH to the metallic Pd NPs to generate a Pd-hydride. Conversely, no primary KIE was observed ($k_H/k_D = 1.0$; Scheme 3) for the addition of PhMe₂SiH with [D1]-**1a** with 89% D-incorporation in the vinylsilane, suggesting that the C-H bond of the terminal alkyne is not cleaved in the catalytic cycle, which thus rules out a possible competing Pd-vinylidene based pathway, as proposed in some transition-metal-catalyzed hydrosilylation reactions.²⁵



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Scheme 4. Proposed mechanism for alkynes hydrosilylation catalyzed by Pd@N,O-Carbon with iodide ion.

Given the mixture of stererodivergent formation with the predominant thermodynamically stable β -(E)-vinylsilane as major products obtained in all cases with combination of the above control experimental results, we propose the classic Chalk-Harrod mechanism is operating in the present catalysis system as shown in Scheme 4. However, further studies to elucidate the key role of I^- in each step of the entire catalytic cycle are strongly required.

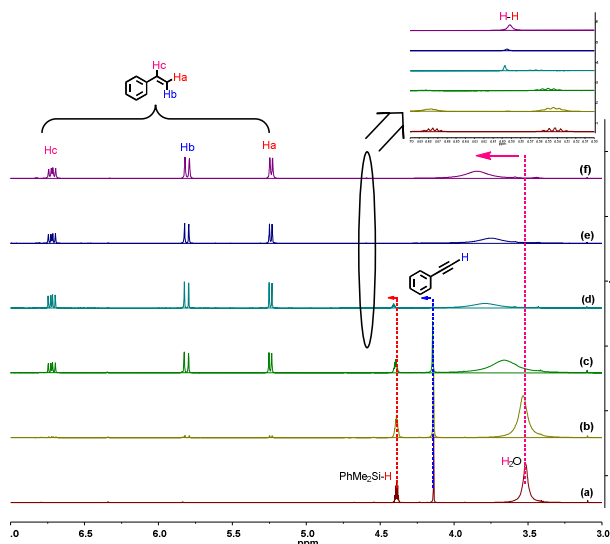
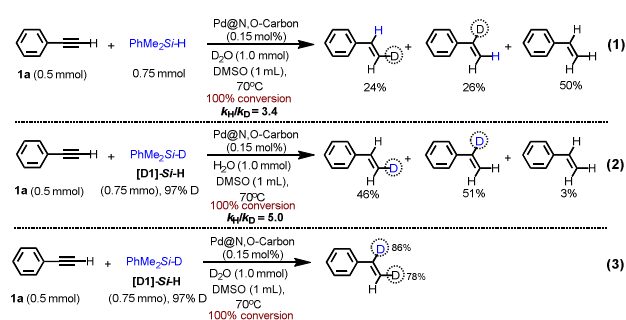


Figure 3. In-situ NMR experiment for phenylacetylene transfer semihydrogenation with PhMe_2SiH and H_2O in d_6 -DMSO at 70°C . (a) the reaction mixture in the absence of Pd@N,O-Carbon. (b) the reaction mixture with Pd@N,O-Carbon at 1 min. (c) at 10 min. (d) at 25 min. (e) at 35 min. (f) at 50 min.

We further investigated the possible mechanism of transfer semihydrogenation of alkynes catalyzed by Pd@N,O-Carbon using the mixture of hydrosilane and H_2O as hydrogen donor. More recently, the hydrolytic or alcoholic oxidation of silanes is a hot topic that has received considerable attention. Several metal NPs such as Ag ,²⁶ Au ,²⁷ and Pd ²⁸ have been developed for such oxidation transformation with high efficiency to the corresponding silanols. Note that dihydrogen gas is concomitantly generated stoichiometrically in these cases, which offers desirable hydrogen source for semihydrogenation of alkynes.

To determine whether the hydrogen donor sources for alkyne semihydrogenation come from the in-situ generated H_2 gas or other H species, we first exploited the oxidation reaction of PhMe_2SiH with water catalyzed by the catalyst Pd@N,O-Carbon. Indeed, this is the case that PhMe_2SiOH was generated efficiently together with evolution of stoichiometric H_2 gas confirmed by GC-MS and ^1H NMR as shown in Figure S3. However, when the catalyst Pd@N,O-Carbon was added into the reaction mixture (including **1a**, PhMe_2SiH and water in d_6 -DMSO), we didn't observe any evolution of H_2 gas, suggesting that the difference of two reaction pathways involved. In latter case, the in-situ NMR experiment (Figure 3) showed that the

respective ^1H NMR peak for each substrate shifted to low magnetic field, and such shift was kept gradually along with the consumption of each substrate. More interestingly, the new peak at 4.6 ppm, assignable to in-situ generated H_2 ,²⁹ started to appear when **1a** was approaching complete conversion, while no such peak was observed if **1a** still presented. Such observations clearly indicate that: 1) each substrate indeed chemically interacts with Pd NPs, which results in the chemical shifts; 2) two pathways of semihydrogenation of alkyne against liberation of H_2 gas compete each other. In other words, the reaction of alkyne with hydrogen atoms on Pd NPs surface, which were in-situ generated from the interaction of Si-H and H_2O with Pd NPs, to produce alkene is governed without evolution of H_2 firstly, whereas the hydrogen atoms rapidly associate together to liberate H_2 gas once complete consumption of alkyne.

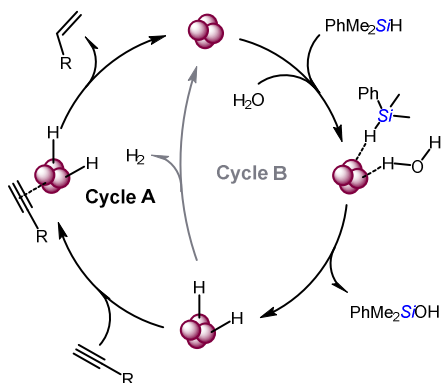


Scheme 5. Deuterium labeling experiments.

To gain further insight into reaction details, we carried out the deuterium labeling experiments (see Supporting Information for details). The reaction of alkyne **1a** with PhMe_2SiH and D_2O in the presence of the catalyst Pd@N,O-Carbon in anhydrous DMSO proceeded more slowly to give a mixture of α -D- and β -D-incorporated styrene together with none-D-incorporated one, respectively. The α - and β -D-incorporated styrene was concomitantly generated most likely accounts for the occurrence of H/D scrambling between D_2O and PhMe_2SiH under reaction conditions. A relatively larger KIE value ($k_H/k_D = 3.4$, Scheme 5) was observed in this case, indicating that cleavage of the H-O-H bond takes place in the course of reaction. Likewise, the reaction of **1a** with [D1]- PhMe_2SiD and H_2O catalyzed by Pd@N,O-Carbon also showed considerably lower reaction rate, affording a mixture of α -D- and β -D-incorporated styrene along with a small amount of none-D-incorporated one. In this case, a typical primary KIE value ($k_H/k_D = 5.0$, Scheme 5) was detected, indicative of the cleavage of Si-H bond during the reaction. In addition, when PhMe_2SiD and D_2O were used, two D atoms were incorporated into the styrene in high yield without any formation of H/D scrambling styrene. These results clearly indicate that the hydrogen atoms on the formed alkenes were derived from PhMe_2SiH and water, respectively.

On the basis of these control experimental observations and combined with the previously reported results, we proposed the reaction mechanism operates for the present catalytic transfer semihydrogenation as shown in Scheme 6. Initially, hydrosilane Si-H and H_2O get adsorbed onto the Pd NPs and were activated to form

hydrogen atoms on Pd NPs surface, which can sequentially react with the adsorbed alkyne to produce the desired alkene (Cycle A). Once full consumption of alkyne or in the absence of alkyne, the hydrogen atoms on Pd NPs surface may rapidly associate together to liberate H₂ gas (cycle B), which is in good agreement with the observation of in-situ ¹H NMR experiment.



Scheme 6. Reaction Pathways for the Pd@N,O-Carbon Catalyzed Transfer Semihydrogenation of Alkynes.

Conclusions

In summary, we developed a highly efficient and robust heterogeneous supported Pd NPs on N,O-dual-doped hierarchical porous carbon derived from naturally renewable bamboo shoots. The catalyst allows for the addition of alkynes with hydrosilanes to afford the corresponding versatile vinylsilanes and alkenes in high yields with excellent chemo-, regio-, and stereo-selectivity under ambient conditions. Two reaction pathways can be readily controlled by simple modification of additive. A broad set of alkyl and aryl alkynes could be efficiently hydrosilylated or semihydrogenated to the corresponding vinylsilanes or alkenes with good functional groups tolerance. The catalyst also demonstrates strong stability for both transformation reactions, can be easily recovered for successive uses.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Additive-Modulated Switchable Reaction Pathway in the Addition of Alkynes with Organosilanes Catalyzed by a Supported Pd Nanoparticles: Hydrosilylation versus Semihydrogenation

Yanan Duan, ^{†a} Guijie Ji, ^{†a} Shaochun Zhang, ^{*a} Xiufang Chen ^a and Yong Yang ^{*a}

