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Pd Nanoparticles and Aminopolymers Confined in Hollow Silica Spheres as Efficient and Reusable Heterogeneous Catalysts for Semihydrogenation of Alkynes

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ABSTRACT: A yolk-shell nanostructured composite composed of Pd nanoparticles (NPs) and aminopolymers, poly(ethyleneimine) (PEI), confined in hollow silica spheres which act as an efficient and stable heterogeneous catalyst for semihydrogenation of alkynes is reported herein. The yolk–shell nanostructured Pd-PEI-silica composite catalysts (Pd+PEI@HSS), consisting of Pd NPs core ca. 5–9 nm in diameter and a porous silica shell ca. 30–50 nm in shell thickness, are fabricated by a facile one-pot method using linear- or branched-type PEI ($M_w = 1,800-2,500$) as an organic template. On the basis of comprehensive structural analyses by FE-SEM, TEM, N₂ physisorption, IR, TG, and Pd K-edge XAFS, we show that metal Pd NPs and PEI molecules are encapsulated in the hollow silica sphere with a size of ca. 100–160 nm. The Pd+PEI@HSS composite shows an activity at near room temperature in the liquid-phase hydrogenation of diphenylacetylene to selectively produce *cis*-stilbene with 95% yield, which outperforms those of the previously-reported Pd/PEI and Lindlar catalysts. Interestingly, the catalyst encapsulating linear-type PEI provides a markedly high alkene selectivity in the semihydrogenation of phenylacetylene to produce styrene owing to the strong poisoning effect of linear PEI, which is clearly revealed by an isotope study using H₂/D₂/acetylene (or ethylene) gases. The catalyst synthesized with optimum silica shell thickness can be easily recovered and recycled without ant loss of palladium species and PEI and retaining high activities and selectivities over multiple cycles owing to the ability of the protective effect of silica shell, rendering this material an efficient and stable catalyst for semihydrogenation of alkynes.

KEYWORDS: yolk-shell nanostructure, porous materials, Pd nanoparticles, aminopolymer, semihydrogenation

1. INTRODUCTION

Selective hydrogenation of alkynes to produce alkenes is an important and fundamental reaction for the synthesis of commodity chemicals and fine chemicals.1-3 Although a large number of homogeneous/heterogeneous catalysts have been developed for semihydrogenation of alkynes,4-5 overwhelming majority employed for liquid-phase semihydrogenation of alkynes is Pd nanoparticle (NP) catalyst.⁶⁻⁸ The Lindlar catalyst (Pd/CaCO₃ treated by Pb salts) has long been utilized as a benchmark heterogeneous catalyst.9-10 Lead is used as a modifier to promote selective reduction of alkynes to cis-alkenes, and a basic compound such as quinoline is often added as an organic modifier in the reaction solution to retard the subsequent hydrogenation of *cis*-alkenes to alkanes; however, this catalyst suffers from some critical drawbacks such as high toxicity of Pb and the low alkene selectivity toward terminal alkynes. Development of alternative, greener catalysts while achieving high alkene selectivity and acceptable reaction rate has been a grand challenge for this reaction.

Owing to the strong hydrogenation ability of Pd, alkynes are readily over-hydrogenated to give the corresponding undesirable alkanes over naked Pd NPs.¹¹ Selectivity can be improved by controlling the adsorption kinetics of the reactants (i.e. alkynes and alkenes) on Pd surface, which can typically be manipulated by introducing organic modifiers containing N or S atoms that can strongly coordinate on Pd NPs.¹²⁻¹⁵ For example, Pd NPs stabilized with alkylthiol surfactants show different selectivity in the liquid-phase hydrogenation of alkynes and allyl alcohols.¹⁶⁻¹⁷ Addition of dimethyl sulfoxide (DMSO) is known to improve the alkene selectivity by acting as homogeneous modifiers.¹⁸⁻¹⁹ Amine-based dendrimers have been used as effective scaffolds to immobilize Pd NPs to demonstrate selective hydrogenation of alkynes.²⁰⁻²¹ Recently, poly(ethyleneimine) (PEI) emerged as promising supports for Pd NP catalysts.²²⁻ ²⁴ Abundant amine groups in its polymer chain efficiently coordinate and immobilize Pd NPs, enabling chemoselective semihydrogenation of both internal and terminal alkynes to afford the corresponding alkenes in the presence of 1 atm H₂.²²⁻²³ Although these surfactant-capped and polymer-stabilized Pd NPs show efficient and tunable catalytic properties due to their adequate coordination efficiency, the inherent difficulties in separation and leaching of modifiers as well as sintering of Pd species during catalytic use limit their practical application.

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Recently, much effort has been directed toward development of recoverable and reusable heterogeneous catalytic systems with good activity and selectivity.3 Silica has typically been utilized as an inert oxide support to immobilize Pd NPs with good dispersion and stability.^{21, 25-26} Mitsudome et al. synthesized silica-supported Pd NPs covered with alkyl sulfoxide groups-containing silica shell for selective semihydrogenation of internal/terminal alkynes.²⁷ Amine-functionalized silicas have been used to immobilize Pd NPs due to a strong metal-support interaction; however, high alkene selectivity was unachievable without the addition of homogeneous organic modifiers.^{19,} ²⁸ Jones et al. synthesized Pd-PEI-silica composite catalyst by immobilizing Pd NPs into a SBA-15 mesoporous silica functionalized with PEI polymer, which showed excellent activity and selectivity in the liquid- phase hydrogenation of diphenylacetylene.²⁹ However, leaching of amine-functional groups and Pd species during catalytic use through open-ended pores and the associated catalyst deactivation still remain as a major concern.

23 Herein, we envisioned that hollow silica spheres having 24 enclosed cavity spaces could be a reasonable option to im-25 mobilize Pd NPs together with PEI, since the silica shell is 26 expected to act as a protective barrier to circumvent the 27 sintering of Pd NPs and leaching of PEI during the cataly-28 sis, leading to an improved stability and reusability of cat-29 alyst. Hollow silica encapsulating catalytic components in 30 their internal void spaces (so-called "yolk-shell" 31 nanostructures) is emerging category of nanostructured 32 materials.30-37 In most studies on yolk-shell nanostructured 33 catalysts, the enclosed inner void spaces are used for en-34 capsulation of active catalytic components (such as metal 35 NPs,³⁸⁻⁴³ metal oxides,⁴⁴⁻⁴⁶ and metal complexes⁴⁷⁻⁴⁸); how-36 ever, encapsulation of bulky functional polymers for im-37 provement of catalytic performances has rarely been exam-38 ined. Although a number of strategies have been developed 39 for the fabrication of yolk-shell silica nanostructures, most 40 of them requires complex multiple synthetic procedures, 41 such as ship-in-bottle,49 hard templating,50-51 and selective 42 etching approaches.38, 44, 52-53 Furthermore, selective intro-43 duction of PEI polymer with large molecular weight within 44 the confined nanospace of hollow silica via a post-synthetic 45 approach is quite difficult.^{39, 54} In this context, He et al. re-46 cently developed a facile one-pot method to encapsulate 47 metal NPs in hollow silica spheres with a size of about 100 48 nm using poly(acrylic acid) (PAA) as a sole organic tem-49 plate.55 PAA acted as a core template and as a stabilizing 50 agent of the metal NPs through the coordination interaction between the carboxylate groups on the chain ends and 51 52 the empty orbital of the metals, and a silica shell was subsequently created around the PAA-metal NP aggregate to 53 form yolk-shell nanostructured silica particle. This prece-54 dent work inspired us to develop a new method to synthe-55 size hollow silica spheres encapsulating Pd NPs and PEI us-56 ing PEI as an organic template, since PEI also has an ability 57

to strongly coordinate on metal NPs due to the presence of lone pairs on N atoms of amines.²²⁻²³

In this study, we report a synthesis of new type of yolkshell nanostructured composite composed of Pd NPs and aminopolymers, PEI, confined in hollow silica spheres (Pd+PEI@HSS) for selective hydrogenation of alkynes to produce alkenes. The yolk-shell nanostructured catalyst was for the first time fabricated via a facile one-pot synthesis by using linear or branched PEI as a self-template. The resulting composite was found to act as an efficient and reusable catalyst in the semihydrogenation of internal/terminal alkynes in the presence of 1 atm of H₂ while retaining high alkene selectivity and minimizing the unfavorable over-hydrogenation, which far outperformed those achieved on the prototype supported Pd NP catalysts. Kinetic analysis and isotope experiment were examined to understand the role of PEI in tuning the alkene selectivity. Furthermore, leaching and reusability tests were performed to verify the ability of the silica shell to protect the encapsulated components.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Materials. Tetraethoxy orthosilicate (TEOS, 95%), disodium tetrachloropalladate(II) (Na₂PdCl₄, >95%), palladium(II) chloride (PdCl₂, 99%), palladium(II) acetate (Pd(OAc)₂, >97%), sodium borohydride (NaBH₄, >95%), aqueous ammonia solution (28%), methanol (99.8%), ethanol (99.5%), 1,4-dioxane (99.5%) and 8-hexadecyne (>99%) were purchased from Nacalai Tesque Inc. Poly(ethyleneimine) (linear, $M_w = 2,500, 99\%$) and diphenylacetylene (98%) was purchased from Sigma-Aldrich. Poly(ethyleneimine) (branched, $M_w = 600$, 1,800, and 10,000, 99%) was purchased from Alfa Aesar. Phenylacetylene (>97%), methyl phenylpropiolate (>98%), ethyl phenylpropiolate (>97%), phenylpropiolic acid (>98%) and Lindlar catalyst (5% Pd on CaCO₃ poisoned with 2.4-3.0% Pb) as a reference catalyst were purchased from Tokyo Chemical Industry Co., Ltd. 20% H₂/Ar, 20% D₂/Ar, 10% C₂H₂/Ar, and 10% C₂H₄/Ar gas used for gas-phase hydrogenation experiment were purchased from Taiyo Nippon Sanso Corp.

2.2. Characterization. Field-emission scanning electron microscopy (FE-SEM) images were taken with a JEOL JSM-6500F operating at 12.0 kV. Transmission electron microscopy (TEM) images were taken with a Hitachi H-800 FE-TEM operating at 200 kV. Scanning transmission electron microscope (STEM) images and elemental maps were collected on a FEI TITAN80-300 instrument operated with an accelerating voltage of 200 kV and guipped with an EDAX r-TEM/SuperUTW energy-dispersive X-ray detector. The Pd loadings of the samples were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The PEI content of the samples were determined from the thermogravimetric (TG) analysis data measured on a Rigaku Thermo plus EVO2 under a flow of air (30 mL/min) with a ramping rate of 10 °C/min. Infrared (IR) spectra were collected on a JASCO FT/IR-6300 instrument under vacuum using samples diluted with KBr. Nitrogen adsorption-

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desorption isotherms were measured at –196 °C with a MicrotracBEL BELSORP-max system. Prior to measurements, samples were degassed at 120 °C under vacuum for 3 h to vaporize the physisorbed water. The surface area was calculated from the adsorption data in the range $p/p_0 = 0.05$ -0.25 using the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were calculated by using the Barrett–Joyner–Halenda (BJH) method. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer with CuK α radiation ($\lambda = 1.54056$ Å).

The X-ray absorption fine structure (XAFS) measurements for Pd K-edge were performed in fluorescence mode at the BLo1B1 beamline at the SPring-8 (JASRI), Hyogo, Japan. A double Si(111) crystal monochromator was used for energy selection and a Pd foil was used for energy calibration. Fluorescence Pd K-edge XAFS spectra were collected at room temperature with a Lytle detector. The extended X-ray absorption fine structure (EXAFS) data were normalized by fitting the background absorption coefficient. Fourier transformation of k^3 -weighted normalized EXAFS data (FT-EXAFS) from k space to r space was performed over the range of $3.0 \le k$ (Å⁻¹) \le 11.0 to obtain the radial structure functions (RDFs).

22 23 2.3. Preparation of Pd-PEI-Silica Composites (Pd+PEI@HSS). Yolk-shell nanostructured Pd+PEI@HSS 24 composites were synthesized by an one-pot method devel-25 oped based on Stöber method55-56 using linear- or branched 26 PEI as an organic template, as schematically shown in 27 Scheme 1. In a typical procedure, 0.12 g of PEI was dissolved 28 in aqueous ammonia (2.8 mL, 28%) with magnetic stirring 29 at room temperature, and o.8 mL of aqueous solution of 30 Na₂PdCl₄ (20 mg/mL) and 90 mL of EtOH were subse-31 quently added, followed by vigorous stirring for 30 min to 32 obtain a transparent solution (Scheme 1, step 1; see also the 33 Supporting Information, Figure S1a). Next, 2.0 mL of 34 freshly-prepared aqueous NaBH₄ solution (20 mg/mL) (ap-35 proximately 20 equiv. of Pd) was slowly added to obtain 36 brownish suspension (step 2; see also Figure Sıb). To this 37 solution was rapidly added 1.8 mL of TEOS as a Si source 38 under vigorous stirring (step 3), followed by continuous 39 stirring for 6 h at room temperature to ensure silica shell 40 formation (step 4; see also Figure Sic). The resulting pre-41 cipitate was recovered by centrifugation, washed with DI 42 water (50 mL) and EtOH (50 mL), and dried under vacuum 43 overnight to afford Pd+PEI@HSS as a greyish powder. 44

To investigate the impacts of PEI type on the structure and the catalytic performance of the final solid, synthesis was performed by using linear PEI ($M_w = 2,500$) and branched PEI ($M_w = 1,800$), which were denoted as Pd+PEI(L)@HSS and Pd+PEI(B)@HSS, respectively. Furthermore, these samples were calcined at 550 °C in air for 5 h to remove organic components, which were then reduced at 200 °C in a flow of H₂ (20 mL/min) to give Pd(o) NPs encapsulated in hollow silica spheres (denoted as Pd+PEI(L/B)@HSS_cal). To obtain Pd+PEI@HSS with different silica shell thickness, synthesis was also performed by adding varied amounts of TEOS (0.9, 1.35, 1.8, and 2,7 mL) using linear PEI as a template polymer. The thus obtained samples were denoted as Pd+PEI(L)@HSS_X, where X represents the volume of TEOS added in mL.

2.4. Preparation of Pd/PEI. PEI-supported Pd(o) NPs were synthesized according to the method previously reported in literature.²² Typically, o.12 g of linear PEI ($M_w = 2,500$) was completely dissolved in EtOH (90 mL) with magnetic stirring at room temperature, and o.8 mL of aqueous solution of Na₂PdCl₄ (20 mg/mL) was added in Ar atmosphere, followed by ultrasonication and stirring for 10 min. The resulting solution was stirred in a continuous flow of H₂ (10 mL/min) at room temperature for 24 h to yield a black colloidal solution. After removal of EtOH by evaporation, a black gummy Pd/PEI was obtained. The Pd loading is 4.6 wt% based on the incipient ratio of Na₂PdCl₄ and PEI.

2.5. Liquid-phase Semihydrogenation of Alkynes. Catalytic reactions were performed at 30 °C in a schlenk flask connected to a water-cooling condenser under a continuous flow of 1 atm H₂. In a typical reaction procedure, as-prepared Pd+PEI@HSS (ca. 0.05 g: Pd 0.005 mmol) was placed in the flask, and the reactor was purged with H₂ gas for 10 min. Next, alkyne (1.0 mmol) dissolved in MeOH (5 mL) and 1,4-dioxane (5 mL) was injected into the flask via a syringe to initiate the reaction. During the reaction, the reaction mixture was magnetically stirred (600 rpm) at 30± 0.5 °C under a continuous flow of 1 atm H_2 (10 mL/min). A small aliquot of reaction solution was withdrawn and the amounts of reactant and products were quantified by a gas chromatograph (GC; Shimadzu, GC-14B) equipped with a flame ionization detector (FID) and a Zebron ZB-WAX plus capillary column using biphenyl as an internal standard. To examine the catalyst reusability, the spent catalyst was recovered by centrifugation, washed with MeOH, dried under vacuum at room temperature, and then subjected to multiple catalytic cycles.

2.6. Gas-phase Hydrogenation Experiment. Gasphase hydrogenation of acetylene and ethylene in the flow of H_2/D_2 gases was carried out at 120 °C in a temperatureprogrammed desorption (TPD) system (BELCAT-II, MicrotracBEL Corp.). About 0.05 g of catalyst (ca. Pd 0.005 mmol) was mounted in a pyrex reactor and pre-reduced at 120 °C under H₂ flow (20 mL/min) for 30 min. In the initial step, mixed gas of H_2 and D_2 balanced with Ar ($H_2:D_2 = 1:1$ volume ratio, 4.3 kPa H₂, 4.3 kPa D₂, 91.4 kPa Ar) was flowed (total flow: 50 mL/min) under the same temperature condition to check H_2 - D_2 isotope exchange reaction. After approximately 10 min reaction, either C_2H_2 or C_2H_4 simultaneously with $H_2/D_2/Ar$ gas was flowed $((H_2+D_2)/C_2H_2 \text{ (or } C_2H_4) = 1.5 \text{ volume ratio, } 4.3 \text{ kPa } H_2, 4.3$ kPa D_2 , 2.9 kPa C_2H_2 (or C_2H_4), 88.5 kPa Ar) (total flow: 50 mL/min). The generated species (m/z = 3 for HD, m/z = 28-30 for ethylene isotopes, m/z = 30-34 for ethane isotopes) were monitored using an online mass spectrometer (MicrotracBEL BELMass)



Scheme 1. Schematic representation of the synthetic procedure of hollow silica spheres encapsulating Pd NPs and poly(ethyleneimine) (Pd+PEI@HSS).

3. RESULTS AND DISCUSSION

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3.1. Preparation and Characterization of Pd+PEI@HSS composites.

Scheme 1 schematically depicts the synthetic procedure of Pd+PEI@HSS composites using linear- or branched PEI as an organic template. In the first step, a transparent solution was obtained after mixing of PEI and Pd precursor in aqueous ammonia solution (Figure S1a), which immediately turned brown after the addition of NaBH₄ (Figure S1b), indicating that PdCl₄²⁻ ions entrapped by the nitrogen ligands on the polymer chain are reduced to form Pd NP-PEI aggregates. In a following step, a brownish milky suspension was obtained in a few minutes after the addition of TEOS as a Si precursor (Figure Sic), representing the condensation of TEOS to form silicate network around the Pd-PEI aggregates as nuclei, which is catalyzed by NH₃ added in the solution as a base. The supernatant solution collected after the recovery of the solid was colorless, suggesting that nearly all of Pd had been incorporated in the product.



Figure 1. (a, d) FE-SEM images, (b, e) TEM images and (c, f) magnified TEM images of Pd+PEI@HSS synthesized with (a-c) linear PEI ($M_w = 2,500$) and (d–f) branched PEI ($M_w = 1,800$).

FE-SEM images show that Pd+PEI@HSS is composed of spherical silicas with an average particle size of ca. 155 nm

and 107 nm for Pd+PEI(L)@HSS and Pd+PEI(B)@HSS, respectively, which are interconnected with each other (Figure 1a and d). TEM images clearly show that the silica spheres have hollow nanostructure with an silica shell thickness of ca. 49 nm and 36 nm for Pd+PEI(L)@HSS and Pd+PEI(B)@HSS, respectively, and Pd NPs are observed in their hollow spaces (Figure 1b,c,e and f) (for the distribution diagrams of silica particle size, silica shell thickness, and Pd NP size, see Figure S₂). Hollow silica particles without encapsulating Pd NPs were scarcely observed. This indicates that silica formation is directed by the preformed Pd-PEI aggregates as nuclei as well as the electrostatic interaction between amine groups on the polymer chain and TEOS.55 Branched-type PEI afforded smaller silica particles with thinner silica shells, which might be due to the lower molecular weight of PEI than that of linear PEI used for synthesis. The average diameter of Pd NPs was determined to be ca. 8.9 nm and 6.0 nm for Pd+PEI(L)@HSS and Pd+PEI(B)@HSS, respectively; however, no clear characteristic peaks for Pd species were observed in XRD patterns, indicating that Pd NPs are highly dispersed (for XRD patterns, see Figure S₃).

The morphology of final solid was strongly dependent on the molecular weight of PEI and the kind of Pd precursor employed; branched PEI with smaller molecular weight $(M_w = 600)$ gave solid silica spheres without hollow cavities (Figure S4a). Use of branched PEI with larger molecular weight (M_w = 10,000) resulted in the formation of amorphous silica without any defined nanostructure (Figure S4c). When other Pd(II) precursors, such as H_2PdCl_4 or $Pd(OAc)_2$ were used, aggregates of small silica particles with ununiformlly-distributed Pd NPs were obtained (see Figure S5). Thus, appropriate choice of PEI and Pd precursor is needed to synthesize yolk-shell nanostructured Pd-PEI-silica composite, since the coordination interaction between Pd species and amine sites on PEI polymer differs depending on the kind of Pd precursor, and the size of Pd-PEI aggregate can be varied depending on the molecular weight of PEI.

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Figure 2. (a) STEM image, (b) High-angle annular dark-field STEM (HAADF-STEM) image, (c-f) the corresponding STEM elemental maps of (c) Pd, (d) Si, (e) O, and (f) N of Pd+PEI(L)@HSS. (g) STEM elemental line scan across the Pd+PEI(L)@HSS particle in (b).

Table 1. Compositional and	Textural Properties of Pd-	PEI@HSS Composites
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Samples		Pd content ^a (wt%)	PEI content ^b (wt%)	N₂ physisorption		
	Ры туре			S_{BET^c} (m ² /g)	$V_{\rm total}^{\rm d}({\rm cm}^3/{\rm g})$	D ^e (nm)
Pd+PEI(L)@HSS	Linear, $M_w = 2,500$	1.1	24.0	34	0.12	2.7
Pd+PEI(L)@HSS_cal	-	1.5	0	19	0.09	2.8
Pd+PEI(B)@HSS	Branched, $M_w = 1,800$	1.1	21.9	35	0.16	2.8
Pd+PEI(B)@HSS_cal	-	1.4	0	28	0.15	2.6
Lindlar catalyst ^f	-	5.0	0	30	0.09	2.7

^{*a*} Determined by ICP-AES. ^{*b*} Determined by TG analysis. ^{*c*} Surface area calculated by BET method. ^{*d*} Total pore volume reported at $p/p_0=0.99$. ^{*e*} Peak pore size determined by BJH method. ^{*f*} 5% Pd on CaCO₃ (poisoned with 3% Pb).

In the HAADF-STEM micrograph of Pd+PEI(L)@HSS (Figure 2), Pd NPs with more electron density located inside the hollow cavities, mostly on the inside silica wall, are clearly observed (Figure 2b). Whole area mapping analysis visualizes that the distributions of Si atoms with blue dots (Figure 2d) and O atoms with pink dots (Figure 2e) overlap with the shell region, and Pd atoms with yellow dots (Figure 2c) are seen in the hollow region, again evidencing the formation of yolk-shell nanostructure consisting of Pd NPs as a core and silica as a shell. N atoms with white dots (Figure 2f) are uniformly distributed throughout the particles, indicating that the PEI is incorporated in both shell and hollow regions. The line mapping of a selected silica particle confirms the inclusion of N, C and Pd atoms in the same axial region (Figure 2g), suggesting a close proximity betwen Pd NPs and PEI.

In FT-IR spectra of Pd+PEI@HSS (Figure 3A), the IR bands at 2962 and 2858 cm⁻¹ assigned to the stretching vibration of aliphatic C–H bond, the band at 1467 cm⁻¹ assigned to the bending vibration of C–H bond, and the peak at 1560 cm⁻¹ assignable to the bending vibration of N–H bond are observed, which completely disappear after thermal treatment at 550 °C in air, further ascertaining the successful incorporation of PEI in the as-synthesized material. The PEI contents were estimated to be 24.0 and 21.9 wt% for Pd+PEI(L)@HSS and Pd+PEI(B)@HSS, respectively, from thermogravimetric (TG) data (Figure 3B), and the Pd contents were determined to be 1.1 wt% in both cases (see Table 1) by elemental analysis, confirming the majority of Pd and PEI added during the synthesis was incorporated in the final solid.

The porous structure of Pd+PEI@HSS materials was investigated by N₂ physisorption measurement. A clear hysteresis observed in the range of $0.4 < p/p_0 < 1.0$ in N₂ adsorption-desorption isotherms indicates the existence of hollow cavities surrounded by mesopore systems (Figure 3C).57 The pore size distributions calculated by the BJH method confirm the existence of broadly-distributed mesopores with average pore size of ca. 2.7 nm (Figure 3D) probably due to the formation of hydroxylated amorphous silica network. The textural properties obtained from the N₂ physisorption analysis are listed in Table 1. BET surface area (S_{BET}) and total pore volume (V_{total}) were determined to be 34 m²/g and 0.12 cm³/g for Pd+PEI(L)@HSS and 35 m^2/g and 0.16 cm³/g for Pd+PEI(L)@HSS, showing that the type of PEI had little influence on the porous structures of the final solid. Nitrogen adsorption data of calcined samples (i.e. Pd+PEI(L)@HSS_cal and Pd+PEI(L)@HSS cal) shows substantial decreases in surface area and pore volume (Table 1), which might be due

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Figure 3. (A) FT-IR spectra of (a) PEI(L), (b) Pd+PEI(L)@HSS, and (c) Pd+PEI(L)@HSS_cal. (B) Weight loss curves, (C) N₂ adsorption-desorption isotherms, and (D) the corresponding pore size distribution curves determined by BJH method for as-synthesized Pd+PEI@HSS composites.

Figure 4A and 4B show X-ray absorption near-edge spectra (XANES) and RDFs obtained from the k^3 -weighted Pd K-edge EXAFS oscillations of the prepared samples, respectively, together with those of reference Pd samples. The X-ray absorption edges of the Pd+PEI@HSS samples $(E_0 = 24355.5 \text{ eV})$ are positioned between the absorption edges of Pd(o) foil ($E_0 = 24352.1$ eV) and Pd(II)O ($E_0 =$ 24358.3 eV), and the height of white line intensity increases in the order of Pd(o) foil < Pd+PEI(L/B)@HSS < Pd(II)O (Figure 4A), indicating the coexistence of Pd(o) and Pd(II) species in the Pd+PEI@HSS samples. In the RDFs of Pd Kedge EXAFS spectra, both Pd+PEI@HSS samples exhibit two distinct peaks at around r = 1.6 and 2.5 Å (the phase shift uncorrected); the first shell at around r = 1.6 Å is associated with the backscattering due to the neighboring nitrogen or oxygen atoms and the second shell at around r = 2.5 Å is attributable to the Pd–Pd bond (Figure 4B). Since the peak ascribed to Pd-O-Pd bond, which typically appear at around r = 3.0 Å, is scarcely observed, the former peak (at r = 1.6 Å) can dominantly be ascribed to the Pd(II) species ligated to the nitrogen moieties of the polymer framework.58 These results, combined with elemental mapping analysis, indicate that the Pd species encapsulated inside hollow silica are primarily present as Pd(o) NPs of which surface is closely surrounded by PEI polymers. The XAFS result also suggests that the the oxidation state of Pd species does not markedly vary depending on the type of PEI used.



Figure 4. (A) Pd K-edge XANES spectra and (B) radial distribution functions (RDFs) obtained from Pd K-edge EXAFS oscillations for Pd+PEI@HSS composites and reference Pd samples.

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Photon energy / eV

3.2. Catalytic Performance of Pd+PEI@HSS composites.

The synthesized Pd+PEI@HSS catalysts were initially assessed in the semihydrogenation of diphenylacetylene (1) with 0.5 mol% Pd in a flow of atmospheric pressure of H₂ at 30 °C. The reaction profiles over the Pd+PEI@HSS catalysts, the calcined analogues and some supported Pd catalysts are shown in Figure 5. The hydrogenation of diphenylacetylene readily took place without any induction period, indicating that Pd species encapsulated in Pd+PEI@HSS samles are predominantly present as metallic Pd(o) NPs as confirmed by Pd K-edge XAFS. Surprisingly, the as-synthesized Pd+PEI(L/B)@HSS catalysts both selectively afforded *cis*-stilbene (2) with >90% selectivities due to the syn-addition of H atoms over Pd(o) NPs surface, and *trans*-stilbene (3) and bibenzyl (4) were hardly produced even after the complete consumption of diphenylacetylene (Figure 5A and C). On the other hand, cis-stilbene was quickly transformed into bibenzyl after the complete conversion of diphenylacetylene over the Pd+PEI(L/B)@HSS calcined in air, PEI-free analogues (Figure 5B and D). This result clearly demonstrates that PEI is capable of efficiently suppressing the over-hydrogenation of stilbene to bibenzyl owing to the strong coordination ability onto Pd NP, which is confirmed by XAFS analysis. It is worth mentioning that the calcined catalysts both showed obviously faster hydrogenation rates compared with the as-synthesized catalysts, due to the removal of PEI covering the surface of Pd NPs. Considering the fact that Pd NPs are the sole active component existing in the present catalytic systems, Pd NPs inside the hollow silica spheres are accessible to reactants through ill-defined mesopores created in the silica shell, and PEI protects the Pd NPs without fully preventing the access to the reactants. Pd+PEI(B)@HSS provided a slightly faster reaction rate compared with Pd+PEI(L)@HSS, which might be explained by the formation of thinner silica shell (36 nm vs. 49 nm) and smaller Pd NP size (6.0 nm vs. 8.9 nm).

Table 2. Comparison of Catalytic Performances of Pd+PEI@HSS Catalysts and Lindlar Catalyst

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Interatomic distance / Å

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Samples	NLa	N _{surf} ^b (mmol/g)	Hydrogenat	Hydrogenation of diphenylacetylene			Hydrogenation of phenylacetylene		
	(mmol/g)		R _Y ^c (h ⁻¹)	$\frac{R_{\rm E}^{\rm d}}{(\rm h^{-1})}$	$R_{ m Y}/R_{ m E}$	R _Y ^c (h ⁻¹)	$\frac{R_{\rm E}^{\rm d}}{({\rm h}^{-1})}$	$R_{\rm Y}/R_{\rm E}$	
Pd+PEI(L)@HSS	0.103	0.0016	4693	< 1	N/A	4111	260	15.8	
Pd+PEI(L)@HSS_cal	0.141	0.0110	770	343	2.25	594	910	0.65	
Pd+PEI(B)@HSS	0.103	0.0020	3065	< 1	N/A	4016	4555	0.88	
Pd+PEI(B)@HSS_cal	0.132	0.0135	1758	2809	0.63	6751	8408	0.80	
Lindlar catalyst	0.470	0.0566	1510	82	18.4	1866	1952	0.96	

^{*a*} Number of Pd atoms contained per gram of catalyst. ^{*b*} Number of surface-exposed Pd atoms contained per gram of catalyst. Determined by CO pulse measurement with MicrotracBEL BEL-METAL-1 system at 50 °C using 1% CO/He gas. ^{*c*} Hydrogenation rate of alkyne calculated from the slope of the initial stage of reaction (conversion < 50%); $R_{\rm Y}$ = (mol of alkyne consumed)/(mole of surface Pd atoms × time). ^{*d*} Hydrogenation rate of alkene calculated from the slope of the initial stage of reaction (conversion < 50%); $R_{\rm E}$ = (mol of alkene consumed)/(mole of surface Pd atoms × time).



Figure 5. Reaction kinetics in the semihydrogenation of diphenylacetylene over (A) Pd+PEI(L)@HSS, (B) Pd+PEI(L)@HSS calcined in air, (C) Pd+PEI(B)@HSS, (D) Pd+PEI(B)@HSS calcined in air, (E) Pd/PEI(L), and (F) Lindlar catalyst (+5 mol% quinoline). *Reaction conditions*: catalyst (Pd o.5 mol%), **1** (1 mmol), MeOH:1,4-dioxane = 1:1 (10 mL), 30 °C, under a flow of 1 atm H₂ (10 mL/min). 5 mol% quinoline was added for Lindlar catalyst.

The Lindlar catalyst (with 5 mol% quinoline) as a benchmark catalyst provided 94.1% selectivity toward *cis*-stilbene in 70 min of reaction, but afterward showed a gradual decrease of selectivity due to the over-hydrogenation into bibenzyl (Figure 5F). Pd/PEI(L) as a

silica-free analogue provided an excellent alkene selectivity (96% (*cis* : *trans* = 97 : 3)), but the reaction rate was apparently lower than that of Pd+PEI(L)@HSS, probably due to the larger size of Pd NPs (Figure 5E).

Hydrogenation rates per surface Pd atoms were calculated based on the number of surface-exposed Pd atoms determined by CO pulse measurement, which are summarized in Table 2. The hydrogenation rate of diphenylacetylene per surface Pd $(R_{\rm Y})$ was calculated to be 3065 h⁻¹ for Pd+PEI(L)@HSS 4693 and and Pd+PEI(B)@HSS, respectively, which were higher than that of Lindlar catalyst (1510 h⁻¹) and previously-reported Pd-PEI-silica composite catalyst (3027 h⁻¹).²⁹ In semihydrogenation of alkyne, hydrogenation rate of alkyne relative to that of alkene (R_Y/R_E) can be a good indicator of alkene selectivity. Hydrogenation of *cis*-stilbene was hardly observed over Pd+PEI(L/B)@HSS catalysts ($R_E < 1 h^{-1}$ ¹), which thereby resulted in significantly higher $R_{\rm Y}/R_{\rm E}$ values than others. Thus, the yolk-shell nanostructured Pd-PEI-silica composites developed in this study provide outstanding activity and alkene selectivity in the hydrogenation of internal alkyne, which outperform those of the conventional supported Pd catalysts.

The yolk-shell nanostructured composite catalysts were also applicable to the selective hydrogenation of phenylacetylene (5) as a terminal alkyne (Figure 6). Pd+PEI(L)@HSS and Pd+PEI(B)@HSS catalysts showed phenylacetylene hydrogenation rates $(R_{\rm Y})$ of 4111 and 4016 h⁻¹, respectively, which were similar to those obtained in diphenylacetylene hydrogenation, indicating similar reactivity of Pd atoms toward internal and terminal alkynes. A marked difference was observed in selectivity of alkene. When Pd+PEI(L)@HSS catalyst synthesized with linear PEI was used, styrene (6) was selectively produced with excellent selectivity (87%), affording 84.3% yield of styrene after 240 min of reaction, and subsequent hydrogenation into ethylbenzene (7) was significantly suppressed even after the complete consumption of phenylacetylene (Figure 6A). Such a retention of high styrene selectivity was not observed for the PEI-removed samples (Figure 6B, D), demonstrating that the surface poisoning of Pd NPs with PEI(L) is the main cause for the improved alkene selectivity. On the other hand, Pd+PEI(B)@HSS synthesized with branched PEI showed a significant decrease in styrene

selectivity after the complete conversion of phenylacetylene, affording ethylbenzene as a main product (cf. Figure 6C). A silica-free analogue, Pd/PEI(L), showed a similar reaction trend, but showed a lower styrene yield (75.9% at a maximum) and a faster reaction rate in the second hydrogenation step to produce ethylbenzene compared with Pd+PEI(L)@HSS (Figure 6E). Lindlar catalyst was totally ineffective for the selective production of styrene under the identical conditions implemented in this study, giving 100% yield of ethylbenzene after the extended reaction time (120 min) (Figure 6F).

300 100 200 400 500 20 30 40 Time / min Time / min (E) 100 (F) 100 88.49 75.9% 80 80 Yield / % Yield / % 60 60 40 40 20 20 6 250 150 200 100 50 100 150 50 Time / min Time / min Figure 6. Reaction kinetics in the semihydrogenation of phenylacetylene over (A) Pd+PEI(L)@HSS, (B) Pd+PEI(L)@HSS calcined in air, (C) Pd+PEI(B)@HSS, (D) Pd+PEI(B)@HSS calcined in air, (E) Pd/PEI(L), and (F) Lindlar catalyst (+5 mol% quinoline). Reaction conditions: catalyst (Pd 0.5 mol%), 5 (1 mmol), MeOH:1,4-dioxane = 1:1 (10 mL), 30 °C, under a flow of 1 atm H_2 (10 mL/min). 5 mol% quinoline was added for Lindlar

On the basis of difference in reaction kinetics observed, as well as structural and compositional similarity between Pd+PEI(L)@HSS and Pd+PEI(B)@HSS catalysts, it can be hypothesized that linear PEI coordinates and passivates Pd

selectivity, we carried out gas-phase hydrogenation of acetylene and ethylene in a co-flow of H₂ and D₂ under accelerated condition (120 °C), which provided more pronounced product distributions with sufficient signal intensities.12 Time courses of the generated species produced during the H₂-D₂ exchange reaction and the subsequent gas-phase hydrogenation reaction of acetylene and ethylene in the co-flow of H₂ and D₂ over Pd+PEI(L)@HSS, Pd+PEI(B)@HSS, and calcined Pd+PEI(L)@HSS are summarized in Figure 7. Under the continuous flow of H₂ and D_2 , H_2 - D_2 exchange reaction to produce HD (m/z = 3) took place over all three types of catalysts, evidencing that dissociative adsorption of $H_2(D_2)$ on Pd NPs are possible even in the presence of PEI. Production of a larger quantity of HD over calcined Pd+PEI@HSS is due to the removal of protective PEI ligand. After the introduction of acetylene (Figure 7A), substantial formations of ethylene isotopes (nondeuterated and deuterated, m/z = 28-30) and ethane isotopes (nondeuterated and deuterated, m/z = 30-34) were observed along with the decreased HD formation over calcined Pd+PEI(L)@HSS catalyst. Pd+PEI(B)@HSS catalyst showed an apparently decreased formation of ethane, which however was not fully prevented. On the other hand, ethane was hardly produced over Pd+PEI(L)@HSS catalyst, representing a discriminative adsorption of acetylene over ethylene. Furthermore, in the co-flowing of ethylene with H_2/D_2 (Figure 7B), substantial amount of ethane isotopes (m/z = 30-32) were produced over calcined Pd+PEI(L)@HSS catalyst; however, ethane species were scarcely detected over Pd+PEI(L/B)@HSS catalysts, showing that adsorption of ethylene on these catalysts are negligible. These results clearly evidence that linear PEI more strongly coordinates on Pd NPs than branched PEI does, thereby more effectively prohibiting the adsorption of ethylene with weaker binding energy on Pd NPs (ethylene binding energies on Pd(111): -82 kJ/mol), while allowing the adsorption of acetylene with stronger binding energy on Pd NPs (acetylene binding energy on Pd(111): -136 kJ/mol).⁵⁹ We believe that the different coordination ability of PEI is derived from molecular structure of PEI, i.e. the steric hindrance effect on the amine sites;⁶⁰ Linear PEI, almost exclusively composed of secondary amines with less steric hindrance, can coordinate on Pd NPs more effectively, whereas branched PEI, containing primary, secondary, and tertiary amines, has a reduced ability to coordinate on Pd NPs due to the considerable steric hindrance around the tertiary amine sites.⁶¹ Thereby linear PEI allows discriminative adsorption of alkynes over alkenes and prevents the over-hydrogenation, thus leading to an increased alkene selectivity. It is also worth mention-

ing that Pd+PEI(L/B)@HSS catalysts are thermally stable

up to at least 120 °C with retaining high alkene selectivity.

NPs more effectively than branched PEI does. In order to

clarify the difference of PEI polymers in controlling alkene

catalyst.





Figure 7. Time courses in H_2 - D_2 exchange reaction and the subsequent gas-phase hydrogenation of (A) acetylene (C_2H_2) and (B) ethylene (C_2H_4) in a co-flow of H_2 and D_2 over as-synthesized Pd+PEI(L)@HSS, as-synthesized Pd+PEI(B)@HSS and calcined Pd+PEI(L)@HSS.

3.3. Impacts of Silica Shell Thickness on Catalytic Performance.

In order to investigate the impacts of the silica shell thickness on catalytic performances, an array of Pd+PEI(L)@HSS catalysts with different silica shell thickness were prepared simply by changing the volume of TEOS added during the synthesis, and examined in the Figure semihydrogenation reactions. 8A shows representative TEM images of Pd+PEI(L)@HSS synthesized with varied volumes of TEOS (0.9 - 2.7 mL). The textural properties determined from TEM images are tabulated in Table 3 (for the distribution diagrams of silica particle size, silica shell thickness, and Pd NP size, see Figure S7). Similar yolk-shell nanostructured Pd-PEI-silica

composites were obtained when more than 1.35 mL of TEOS was added per 0.12 g of PEI, while addition of less amount of TEOS (0.9 mL) resulted in the formation of solid silica particles without defined hollow structure (Figure 8Aa). As increasing the TEOS volume from 1.35 mL to 2.7 mL, larger silica particles with a thicker silica shell and a narrower inner space were obtained; the average silica shell thickness increased from 29 nm (TEOS: 1.35 mL), 49 nm (TEOS: 1.8 mL) to 74 nm (TEOS: 2.7 mL) (Figure 8A(b-d)). The Pd NPs were found to be in the range of 5.0-9.0 nm in diameter. The BET surface area and total volume decreased along with the increased volume of TEOS added, which can be interpreted by the increased volume fraction of silica shell relative to that of inner void space.

Table 3. Textural Properties of Pd+PEI(L)@HSS Composites Synthesized with Varied TEOS Volumes

Samples	TEOS added (mL)	PEI content ^a (wt%)	Average silica particle size ^b (nm)	Average silica shell thickness ^b (nm)	Average Pd particle size ^b (nm)	N₂ physisorption		
						$\frac{S_{\rm BET}^{\rm c}}{({ m m}^2/{ m g})}$	V _{total} d (cm³/g)	D ^e (nm)
Pd+PEI(L)@HSS_0.9	0.9	27.8	95	N.D.	5.6	41	0.16	2.6
Pd+PEI(L)@HSS_1.35	1.35	24.8	98	29	5.7	42	0.17	2.8
Pd+PEI(L)@HSS_1.8	1.8	24.0	155	49	8.9	34	0.12	2.7
Pd+PEI(L)@HSS_2.7	2.7	23.2	173	74	7.5	24	0.08	2.6

^{*a*} Determined by TG analysis. ^{*b*} Determined by TEM observation. ^{*c*} Surface area calculated by BET method. ^{*d*} Total pore volume reported at $p/p_0=0.99$. ^{*e*} Peak pore size determined by BJH method.



Figure 8. (A) TEM images and reaction kinetics in the semihydrogenation of (B) diphenylacetylene and (C) phenylacetylene over a series of Pd+PEI(L)@HSS synthesized with different volume of TEOS; (a) 0.9 mL, (b) 1.35 mL, (c) 1.8 mL, and (d) 2.7 mL. *Reaction conditions*: catalyst (Pd 0.5 mol%), alkyne (1 mmol), MeOH:1,4-dioxane = 1:1 (10 mL), 30 °C, under a flow of 1 atm H₂ (10 mL/min).

The catalytic performance of the series of Pd+PEI(L)@HSS catalysts were assessed in the semihydrogenation of diphenylacetylene (Figure 8B) and phenylacetylene (Figure 8C) under the identical conditions demonstrated above. In the semihydrogenation of diphenylacetylene, Pd+PEI(L)@HSS_1.35~2.7 with moderate shell thickness (29~74 nm) selectively afforded *cis*-stilbene with suppressing the over-hydrogenation into bibenzyl (Figure 8B(b-d)), while hydrogenation rates decreased as the shell thickness increased, suggesting that mass transfer in the silica shell region dominates the reaction rate. In the semihydrogenation of phenylacetylene, Pd+PEI(L)@HSS_1.35~1.8 catalysts having moderate shell thickness (29, 49 nm) produced styrene as a main product with 84-91% yield and showed much slower rates in the second hydrogenation step than Pd+PEI(L)@HSS 2.7 catalyst having a thicker silica shell (74 nm) (cf. Figure 8C(bd)). Considering that PEI contents in these samples are almost the same (see Table 3), the most probable cause for the different alkene selectivities observed is the proximity of Pd NPs and PEI confined in the hollow silica particles. As confirmed by STEM elemental mapping images (Figure

2), PEI is not only in the inner cavity spaces but also infiltrated into the silica shell. In the case of Pd+PEI(L)@HSS_2.7 with a thicker silica shell, large fraction of PEI is incorporated into the silica shell and the PEI concentration in the hollow cavity space decreases, therefore the PEI coverage on Pd NPs decreases, thus leading to selectivity. lower alkene In the case of а Pd+PEI(L)@HSS_1.35~1.8 with moderate shell thickness, the proximity between Pd NPs and PEI remains unchanged, thereby results in higher alkene selectivities.

In contrast, Pd+PEI(L)@HSS_0.9 without defined hollow structure gave considerable amounts of alkanes from the initial stage of reaction, and showed a faster reaction rate in the second hydrogenation step than yolk-shell nanostructured analogues (Figure 8B(a), 8C(a)). This is probably due to the segregation of Pd NPs and PEI and leaching of PEI during the reaction. These results again verify that the alkene selectivity in these catalysts is deeply associated with the morphology of silica particles and the configuration between Pd NPs and PEI.

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Figure 9. (A) Leaching test in the semihydrogenation of 1 using Pd+PEI(L)@HSS_1.8 catalyst. The red square symbols show the reaction kinetics after the removal of catalyst at 90 min. (B) Reusability test in the semihydrogenation of 1 using Pd+PEI(L)@HSS_1.8 catalyst. *Reaction conditions*: catalyst (Pd 0.5 mol%), 1 (1 mmol), MeOH:1,4-dioxane = 1:1 (10 mL), 30 °C, under a flow of 1 atm H₂ (10 mL/min), t = 3 h.

The major reasons for deactivation of supported Pd catalysts in liquid-phase hydrogenation is sintering and leaching of active Pd species. In the semihydrogenation of diphenylacetylene, the reaction was immediately quenched after the removal of the catalyst by centrifugation (Figure 9A), ensuring that the catalyst acts a heterogeneous catalyst. To assess the stability and reusability, the catalyst was reused up to five repeated catalytic cycles. Pd+PEI@PEI(L) with an optimum silica shell thickness (ca. 49 nm) exhibited excellent recyclability without any loss of activity and selectivity as well as reaction rate (Figure 9B, for reaction profiles, see Figure S8). ICP analysis also confirmed that Pd content was maintained at 1.1 wt%, proving a negligible leaching of Pd species during the catalytic reactions.



Figure 10. (A) TEM image of Pd+PEI(L)@HSS catalyst after five catalytic runs. (B) Pd K-edge FT-EXAFS spectra, (C) N_2 adsorption-desorption isotherms, and (D) weight loss curves

of Pd+PEI(L)@HSS catalyst before and after five repeated catalytic runs in the semihydrogenation reaction of 1 (the reaction conditions are the same as those described in Figure 9).

The catalyst recovered after five repeated cycles was further characterized by TEM, Pd K-edge XAFS, N₂ physisorption and TG measurements. TEM image clearly shows that the yolk-shell nanostrcture remained intact even after five repeated cycles, and the size of the Pd NPs ($d_{ave} = 8.0 \text{ nm}$) was similar to that of the fresh catalyst ($d_{ave} = 8.9 \text{ nm}$) (Figure 10A). Pd K-edge FT-EXAFS spectrum of the used catalyst exhibited two distinct peaks assignable to Pd-N (r = 1.6 Å) and Pd-Pd bonds (r = 2.5 Å). This result indicates that the coordination between Pd(o) NPs and nitrogen ligands on PEI polymer remains intact. No significant structural change was identified from N₂ adsorption isotherms (surface area was $34 \text{ m}^2/\text{g}$ for fresh catalyst, and $32 \text{ m}^2/\text{g}$ for used catalyst, Figure 10C). In addition, PEI content remained unchanged even after the catalytic reactions (24.0 wt% for fresh catalyst, 23.5 wt% for used catalyst, Figure 10D), indicating the leaching of PEI polymer during the catalytic reaction is negligible as well.

Table 4. Scope of Substrates in the Semihydrogenation of Alkynes with 1 atm H_2 over Pd+PEI(L)@HSS Catalyst^a

Entry	Substrate	Time (min)	Conv. ^b (%)	Alkene Sel. ^b (%)	Z:E ^b
1		270	>99	84	-
2	$\overline{} = \overline{}$	360	>99	95	95:5
3	<он	480	>99	81	94:6
4	√→→→→ ○ Me	360	>99	94	100 : 0
5°		300	>99	76	100 : 0
6	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	180	>99	100	100 : 0

^{*a*}*Reaction conditions*: catalyst (Pd+PEI(L)@HSS, Pd 0.5 mol%), alkyne (1 mmol), MeOH:1,4-dioxane = 1:1 (10 mL), 30 °C, under a flow of 1 atm H_2 (10 mL/min). ^{*b*}Determined by GC-FID. ^{*c*}E-tOH:1,4-dioxane = 1:1 (10 mL) was used as solvent.

Furthermore, Pd+PEI(L)@HSS_1.8 catalyst, the best performance catalyst among examined in this study, provided good selectivity for the semihydrogenation of other alkynes (Table 4). Several kinds of aromatic and aliphatic internal alkynes were efficiently hydrogenated to the corresponding alkenes with good to excellent yields (entries 2– 6) using atmospheric pressure of H₂ as a reductant, while suppressing over-hydrogenation to corresponding alkanes. These results led us to a conclusion that Pd+PEI(L)@HSS catalyst having an optimum silica thickness can act as a stable, reusable, and efficient heterogeneous catalyst in the liquid-phase semihydrogenation of alkynes.

4. CONCLUSIONS

A new type of Pd-PEI-silica composite with yolk-shell nanostructure was developed for the selective hydrogenation of alkynes to produce alkenes. The synthesized composite was composed of Pd NPs core less than 9 nm in diameter and linear/branched PEI which were confined in hollow silica spheres having ill-defined mesoporous structures with a particle size of 100-160 nm. The present synthetic protocol provides a facile one-pot synthetic process for the fabrication of yolk-shell silica nanostructure with tunable size and shell thickness without severe control of synthetic conditions. Such a yolk-shell nanostructured composite could act as an efficient and reusable heterogeneous catalyst in the semihydrogenation of alkynes in the presence of 1 atm H₂, giving a markedly improved alkene selectivity compared with the previously-reported prototype Pd catalysts. In particular, the catalyst encapsulating linear PEI afforded a high alkene selectivity in the semihydrogenation of phenylacetylene to produce styrene, in which silica shell thickness had a strong influence on alkene selectivity. Comprehensive analysis together with isotope experiment revealed that Pd NPs and PEI polymers are encapsulated within the hollow silica particles in close proximity, in which the PEI acts as a macro-ligand to strongly coordinate on Pd NP surface, enabling discriminative adsorption of alkynes over alkenes. This leads to highly selective hydrogenation of alkynes to alkenes with suppressing over-hydrogenation into alkanes. Owing to the rigidity of the protective silica shell, the catalyst was easily recoverable and reusable without leaching of Pd species and PEI, with retaining high activities and selectivities over multiple cycles, rendering this material an efficient and stable catalyst for semihydrogenation of alkynes.

ASSOCIATED CONTENT

Supporting Information.

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This Supporting Information is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

Photographs of synthetic solutions (Figure S1), statistical structural data of samples (Figure S2), XRD patterns (Figure S3), TEM images of samples synthesized with different polymers (Figure S4) or different Pd precursors (Figure S5), N_2 physisorption data upon calcination (Figure S6), statistical structural data of samples synthesized with varied TEOS amounts (Figure S7), and reaction profiles during catalyst reusability test (Figure S8) (PDF)

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Notes

The authors declare no competing financial interest.

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