

Silica-Dendrimer Core-Shell Microspheres with Encapsulated Ultrasmall Palladium Nanoparticles: Efficient and Easily Recyclable Heterogeneous Nanocatalysts

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Supporting Information

ABSTRACT: We report the synthesis, characterization, and catalytic properties of novel monodisperse SiO2@Pd-PAMAM core-shell microspheres containing SiO₂ microsphere cores and PAMAM dendrimer-encapsulated Pd nanoparticle (Pd-PAMAM) shells. First, SiO₂ microspheres, which were prepared by the Stöber method, were functionalized with vinyl groups by grafting their surfaces with vinyltriethoxysilane (VTS). The vinyl groups were then converted into epoxides by using m-chloroperoxybenzoic acid. Upon treatment with amineterminated G4 poly(amidoamine) (PAMAM) dendrimers, the SiO₂-supported epoxides underwent ring-opening and gave SiO2@PAMAM core-shell microspheres. Pd nanoparticles within the cores of the SiO₂-supported PAMAM dendrimers were synthesized by letting Pd(II) ions complex with the amine groups in the cores of the dendrimers and then reducing them into Pd(0) with NaBH₄. This produced the SiO₂@Pd-PAMAM core-shell microspheres. The presence of the



different functional groups on the materials was monitored by following the changes in FTIR spectra, elemental analyses, and weight losses on thermogravimetric traces. Transmission electron microscopy (TEM) images showed the presence of Pd nanoparticles with average size of 1.56 ± 0.67 nm on the surface of the monodisperse SiO₂@Pd-PAMAM core-shell microspheres. The SiO₂@Pd-PAMAM core-shell microspheres were successfully used as an easily recyclable catalyst for hydrogenation of various olefins, alkynes, keto, and nitro groups, giving \sim 100% conversion and high turnover numbers (TONs) under 10 bar H₂ pressure, at room temperature and in times ranging from 10 min to 3 h. In addition, the SiO₂@Pd-PAMAM core-shell microspheres were proven to be recyclable catalysts up to five times with barely any leaching of palladium into the reaction mixture.

1. INTRODUCTION

The use of metal nanoparticles (MNPs) in catalysis has rapidly increased in recent years because of their efficient and intrinsic size-dependent catalytic properties as well as their ability to catalyze a range of chemical reactions.¹⁻⁸ For many MNPs to catalyze reactions or result in efficient catalysis, the reacting substrates must directly interact with the metal surfaces. This metal-substrate interaction would be greater if the MNPs were synthesized "naked". Unfortunately, however, atoms of "naked" MNPs have a greater tendency to aggregate into a bulk material due to their high surface energies, which results in loss of, or decrease in, their intrinsic catalytic activity and selectivity over time.9 In particular, Pd nanoparticles (PdNPs), which are wellknown for their catalytic activities, can easily aggregate to form Pd-black because of the very high surface energy of palladium.¹⁰ Although the degree of aggregation of PdNP or other MNP catalysts can be overcome or minimized by passivating the metals' surfaces with organic ligands,¹¹ this too will, unfortunately, be accompanied by the loss of catalytic activity because

the very sites on the metals where catalysis takes place will be covered by these surface passivating organic groups. The degree of passivation of the surface of metallic nanoparticles can become more optimized for catalysis with dendrimers as stabilizing agents. This is because the branching and porous structures of dendrimers will inhibit them from forming a well-packed selfassembled monolayer (SAM)-like structure that alkanethiol and alkylamine groups typically form around the metallic nanoparticles. Thus, dendrimer-encapsulated metallic nanoparticles can exhibit better catalytic activities compared to other types of ligand-stabilized nanoparticles.

Since the first reports by the groups of Crooks,¹² Tomalia,¹³ and Esumi,¹⁴ dendrimers have indeed been successfully used to stabilize a number of MNPs including PdNPs.¹⁵ Furthermore, the resulting dendrimer-encapsulated nanoparticles (DENs)^{2,16}

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were shown to have various applications in sensing, molecular electronics, photonics, and nanomedicine.¹⁷ In addition, with the pioneering works of Crooks and co-workers, DENs consisting of transition metal nanoparticles within their cores^{12b} were shown to serve as stable nanocatalysts. DEN catalysts, also known as dendrimer-encapsulated catalysts (DECs), have branching structures that allow reactants to diffuse in and reach the entrapped nanoparticle catalytic sites while at the same time stabilize the nanoparticles from aggregation. For instance, Mizugaki et al. recently demonstrated the synthesis and catalytic properties of PAMAM dendron-stabilized PdNPs for hydrogenation of dienes and acetylenes to monoenes.¹⁸ In another example, Ooe et al. synthesized triethoxybenzamide-terminated poly(propyleneimine) (PPI) dendrimer-stabilized PdNPs and showed their use as substrate specific catalysts for hydrogenation reactions.¹⁹

Although the synthesis and catalytic activities of various DECs have been successfully demonstrated, dendrimers, even those with many generations, are relatively too small to easily separate from solutions and reuse after catalytic reactions-a feature that is often sought for "true" heterogeneous catalysts.²⁰ Thus, research in the past several years has also focused on developing easier ways for recycling DECs. Solvent precipitation²¹ and membrane filtration²² were among the common methods considered to separate and recycle DECs; however, they were shown to result in some losses of the materials as well as their catalytic activities. Surface modification of the surfaces of DECs by multi-step chemical reactions in order to tune the DECs' solubility and help their separation from solutions have also been reported.²³ Similarly, dialysis was used to separate dendrimers from solutions.²⁴ However, both surface modification and dialysis involve time-intensive processes and relatively costly reagents and membranes. Although separation of dendrimers by electrophoresis and chromatography is also possible, it is complicated by interaction of dendrimers with the stationary support materials, leading to the retention and incomplete separation of the dendrimers.²⁵ In another work, Crooks group²⁶ used selective solution phase extraction to separate a mixture of DENs containing Ag and Au nanoparticles from each other from an aqueous solution. Similarly, the group led by Baker reported the separation of different generations (G1-G9) of amino-, acetamide-, hydroxyl-, and carboxylate-terminated dendrimers using reversed-phase HPLC.²⁷ Although these two research groups showed elegant methods for separating a mixture of two or more types of dendrimers (or DENs), analyzing them as well as extracting the entrapped MNPs from within the DENs, the methods have limited applications for recycling DECs in catalysis.

Thus, in order to overcome these inherent difficulties in separation and recycling of DECs from solutions, heterogenizing DECs on solid support materials has been receiving increased attention. Recently, Somorjai and Toste groups have introduced a synthetic strategy that involves the immobilization of Gn-PAMAM dendrimer-based DECs containing Pt nanoparticles (PtNPs) within the pores of mesoporous material, SBA-15.28 The resulting material, labeled as Gn-PAMAM-SBA-15, was shown to combine the advantages of both "homogeneous" and "heterogeneous" catalysts and exhibited the "true" features of heterogeneous catalysts.²⁰ However, the long cylindrical channel pores of SBA-15 mesoporous silica support in which the DECs are encapsulated still pose some limitations for reactants to reach all the PtNPs (or the DECs). Moreover, the DECs in this case are noncovalently immobilized in the support material; thus, they are more likely to leach out.²⁹ Covalent attachment of dendrimers or

dendrons onto the surfaces of the channels of mesoporous silicas were achieved using a different synthetic strategy as reported by Jiang and Gao,³⁰ Wang et al.,³¹ and Reynhardt et al.³² In these cases, the dendrimers were synthesized in situ within amine-functionalized SBA-15 by multistep procedures involving the Michael-type addition reaction between the amino groups of the material and methyl acrylate, followed by amidation of the resulting ester groups with ethylenediamine. Furthermore, Jiang and Gao³⁰ used the covalently supported dendrimers to synthesize PdNPs in situ for catalysis. However, this material also has the DENs within the "small" cylindrical channel pores of SBA-15, possibly limiting the reactants access to all of the DENs. Covalent attachment of dendrimers on a more accessible outer surface of relatively polydisperse and small size (average size \sim 40 nm) amorphous silica nanoparticles was demonstrated recently by Hagiwara et al.³³ The resulting supported PAMAMs were used to anchor a metal complex (palladium(II) acetate), and ionic liquids noncovalently for the Suzuki-Miyaura reaction. There have been other examples on silica-supported dendrimers containing metal complexes for heterogeneous catalysis of various reactions, including some of the pioneering works in this area by the groups of Alper and Sayari.^{32b,34} A nice review article in this area, particularly on palladium-containing dendrimers and dendrons, has also recently been published by Andrés et al.²⁹

Other notable examples on supported DECs include the works of Chandler³⁵ and Crooks³⁶ groups. In these cases, metal oxides such as silica, alumina, and titania were used either to support or to encapsulate DENs. The dendrimer shells were then removed by high-temperature treatment during catalyst activation, leaving metal oxide-supported MNPs or catalysts. In a related but slightly different approach, Knecht and Wright used the sol-gel process to encapsulate DENs within silica shell using silicic acid.³⁷ This resulted in \sim 80 nm polydisperse silica nanoparticles containing several randomly distributed DENs composed of PAMAM-entrapped Au nanoparticles or quantum dots within the silica nanoparticles. Many of the DENs in the resulting materials appeared to be visibly buried within a thick layer of silica as seen from their reported transmission electron microscopy (TEM) images.³⁷ The accessibility of the DENs in these materials to external probe molecules or reactants for catalysis is not clear.

Herein we report on the synthesis and highly efficient recyclable catalytic properties of novel SiO₂@Pd-PAMAM core-shell microspheres consisting of etched silica microsphere cores and highly accessible DEN shells. The efficient catalytic activities of the SiO₂@Pd-PAMAM core-shell microspheres are confirmed by their ability to catalyze the hydrogenation of various olefins, alkynes, keto, and nitro groups, yielding \sim 100% conversion with high turnover numbers (TONs) under 10 bar H₂ pressure, at room temperature and in reaction times ranging from 10 min to 3 h. Furthermore, the microspheres are shown to be recyclable catalysts in up to five cycles with barely losing their catalytic activities. The SiO2@Pd-PAMAM core-shell microspheres' high catalytic activity is possibly the result of the accessibility of the DECs or PdNPs on the outer surface in the core-shell nanostructure as well as the stability of the PdNPs. The stability and ease of recyclability of the SiO₂@Pd-PAMAM core-shell microspheres as catalysts are most likely due to the attachment of the DECs on relatively bigger etched SiO₂ microspheres via covalent bonds.

2. EXPERIMENTAL SECTION

Chemicals and Reagents. Anhydrous ethanol, aqueous ammonium hydroxide solution (28%), tetraethyl orthosilicate (TEOS, 98%), Pd/C (1%), sodium borohydride (NaBH₄), *m*-chloroperoxybenzoic acid, styrene, phenylacetylene, potassium hydroxide, cyclohexene, *n*-hexene, acetone, acetyleacetonate, styrene oxide, 4-chloroaniline, *trans*-stilbene, 4-nitrostyrene, acetonitrile, methanol, and sodium tetrachloropalladate(II) (Na₂PdCl₄) were obtained from Sigma-Aldrich. Palladium(II) acetylacetonate (99%) was purchased from Strem Chemicals, Inc. Methylene chloride and hydrochloric acid were obtained from Fisher Scientific. Poly-(amidoamine) (PAMAM) dendrimers (G4) as 10–25% in methanol was obtained from Dendritech NanoTechnologies, Inc., Midland, MI.

Synthesis of Silica Microspheres. The synthesis of the spherical silica microspheres was carried out by following previously reported methods.^{38,39} In a 250 mL plastic bottle, aqueous ammonia solution (10 mL), ethanol (100 mL), and distilled water (3.6 mL) were added and stirred vigorously for 2 min. Then, TEOS (5.84 g) was added into the solution under moderate stirring to hydrolyze TEOS. After 3 h of stirring, the solution was centrifuged and the supernatant was decanted carefully. The precipitate was washed three times with 3×40 mL of 1:1 ethanol/water solution by sonication, centrifugation, and decantation. Finally, the precipitate was dispersed by sonication in 40 mL 1:1 ethanol/water solution. This resulted in 450 nm silica microspheres.

Synthesis of Etched Silica Microsphere Cores (SiO₂). The 450 nm silica microspheres synthesized above were etched with 0.01 M aqueous potassium hydroxide (KOH) solution. This is performed to create nanocorrugated surface and increase the microspheres' surface area and consequently help the microspheres anchor the PAMAM dendrimers more effectively. Typically, 250 mg of the silica microspheres was suspended in 0.01 M KOH solution (100 mL) and stirred for 2 h. The resulting etched silica microspheres were centrifuged, and the supernatant was decanted. The particles were washed three times with 3×20 mL Millipore water via sonication, centrifugation, and decantation. They were then dried in a desiccator under vacuum at room temperature (RT). The etched silica microspheres were labeled as SiO₂.

Grafting Vinyltriethoxysilane (VTS) on the Silica Microspheres. The etched SiO₂ microspheres were dried at 100 °C for 12 h prior to grafting by vinyltriethoxysilane (VTS). In a 500 mL roundbottom flask, 500 mg of the etched SiO₂ microspheres was dispersed in dry toluene (250 mL). VTS (3 mL) was then added into the flask, and the solution was refluxed at 80 °C for 6 h. The resulting vinylfunctionalized silica microspheres were collected by centrifugation and washed via sonication, centrifugation, and decantation using 3×10 mL of toluene, 3×10 mL of methylene chloride, and finally 3×10 mL of ethanol. The precipitate was then dried at RT to produce the vinylsilica microspheres.

Epoxidation of Vinylsilica Microspheres into Vinyl Oxide (**Epoxysilica**) **Microspheres.** In a 200 mL round-bottom flask, 500 mg of the above synthesized vinylsilica microspheres was dispersed in acetonitrile (50 mL). After adding excess *m*-chloroperoxybenzoic acid (500 mg) into the solution, it was stirred at RT for 24 h. The resulting epoxysilica microspheres were collected by centrifugation. After decanting the supernatant, the precipitate was washed three times with acetonitrile (3×10 mL) and then three times with ethanol (3×10 mL) via sonication, centrifugation, and decantation. The resulting vinyl oxide-functionalized silica microspheres were then dried and labeled as epoxysilica microspheres.

Ring-Opening of Epoxy Groups of Epoxysilica Microspheres by Amine Groups of G4 PAMAM Dendrimer. In a 100 mL round-bottom flask 400 mg of above prepared epoxysilica microspheres was mixed with G4 PAMAM dendrimer (0.5 mL) and anhydrous acetonitrile (50 mL), and the solution was stirred for 24 h at RT. The 0.5 mL of 10–25% stock solution of G-4 PAMAM dendrimer in methanol, which was obtained from Dendritech NanoTechnologies, Inc., was calculated to have $3.5-8.8 \mu$ mol of PAMAM. The resulting PAMAM dendrimer-functionalized silica microspheres were collected by centrifugation and washed via sonication, centrifugation, and decantation with anhydrous acetonitrile (50 mL), followed by anhydrous ethanol (50 mL), and let to dry. This produced SiO₂@PAMAM dendrimer core shell microspheres, which were found to have 5.9 μ mol PAMAM/g sample by thermogravimetric analysis (TGA) (see Supporting Information).

Entrapping Palladium Nanoparticles within the PAMAM Dendrimers of SiO₂@PAMAM Core-Shell Microspheres (Synthesis of SiO₂@Pd-PAMAM Core-Shell Microspheres). SiO₂@PAMAM dendrimer core-shell microspheres (250 mg) were dispersed by sonication in distilled water (10 mL). The solution was then treated with 2 M HCl (3 mL) for 30 min at RT, until its pH became 2.00. This was performed in order to quaternize the remaining terminal primary amine groups in the PAMAM shell of the SiO2@PAMAM microspheres. This will, in turn, help the amine groups on the external surface of the core-shell microspheres not to anchor Pd(II) ions and not to lead to the uncontrolled growth of Pd particles on the outer surface of the core-shell microspheres. After this step, 0.05 M K₂PdCl₄-(aq) solution (250 μ L) was slowly added, making the G4 PAMAM dendrimer to palladium(II) ratio 3:5. The solution was stirred at RT for 30 min to let Pd(II) ions anchor within the cores of the PAMAM dendrimers. Then, 1 M NaBH₄(aq) solution (500 μ L) was added. This caused the solution to change its color from yellowish to golden brown, indicating the transformation of Pd(II) to Pd(0) (or Pd nanoparticles). The solid material was separated by centrifugation; washed twice with 2×20 mL distilled water via sonication, centrifugation, and decantation; and then dried at room temperature in a desiccator. The resulted material was labeled as SiO2@Pd-PAMAM core-shell microspheres. The sample was kept in a desiccator until its use in catalytic reactions.

Synthesis of SiO₂@Pd Microspheres. A reference core-shell microsphere, labeled as SiO₂/Pd, containing no PAMAM shell was also synthesized by following a method reported by Wan et al.⁴¹ In a typical synthesis, etched silica microspheres (SiO_2) (100 mg) were dispersed in distilledwater (10 mL) by sonication for 1 min and then treated with 20 wt % aqueous HNO3 for 24 h. After filtration, the particles were washed with distilled water. After drying overnight at 110 °C, the resulting SiO₂ microspheres (100 mg) were stirred with Pd(II) acetylacetonate/ acetylacetone solution (2 mL) at room temperature for 24 h. The concentration of Pd(II) ions with respect to SiO₂ microspheres was set to 0.05 wt % Pd in order to produce small size Pd(0) nanoparticles, as reported in ref 41. The solvent was then slowly evaporated at 110 °C under stirring. The obtained solid was dried overnight at 110 °C and then calcined in air at 800 °C for 4 h. Before the sample was used in catalysis, it was treated with NaBH4 in order to reduce any PdO, possibly formed on the sample's surface during and after synthesis, into Pd(0). The solid sample was then let to dry at RT resulting in SiO2@Pd microspheres, which were kept in a desiccator until use in catalytic reactions.

Catalytic Hydrogenation Reaction. The hydrogenation reactions were carried out in a 50 mL high-pressure reactor (Parr Instrument Co.). The reactor was equipped with a heating arrangement, overhead stirrer, thermowell, and pressure gauge as well as a transducer, a gas inlet, a gas outlet, and a sampling valve. The reactor has controllers to set temperatures, pressure and agitation speeds to maximum values of 350 °C, 4000 psig pressure and 1500 rpm, respectively. The reactor was charged with reactant (0.01 mol), methanol (20 mL), and SiO₂@Pd-PAMAM core-shell microsphere catalyst (or control sample) (5 mg) and tightly closed, leak-proof. The reactants included styrene, phenylacetylene, cyclohexene, n-hexene, acetone, acetyleacetonate, styrene oxide, 4-chloroaniline, trans-stilbene, and 4-nitrostyrene. The reactor was flushed three times with nitrogen and then three times more with hydrogen before each reaction. Then hydrogen gas was introduced into the reactor to the desired pressure, and the heater was turned on to achieve the desire reaction temperature under a slow stirring rate at \sim 100 rpm for uniform heat distribution. After attaining the desired



Scheme 1. Synthesis of SiO₂@Pd-PAMAM Dendrimer Core-Shell Microsphere Catalysts

temperature, the reaction was initiated by increasing the agitation speed to 500 rpm. The absorption of hydrogen gas due to reaction was monitored from the pressure drop in the reactor. The reaction was stopped when the gas absorption ceased. The reactor was cooled, and the reaction mixture was analyzed by gas chromatography (GC) and gas chromatography—mass spectrometry (GC-MS).

Instrumentation. FTIR spectra were obtained from samples loaded onto a KBr disk (25×4 mm) using a Thermo-Nicolet IR200 spectrometer. Thermogravimetric analysis (TGA) was performed using a TA Q50 thermogravimetric analyzer with a temperature ramp of 10 °C/min from room temperature to 780 °C under nitrogen gas flow. The UV-vis diffuse reflectance spectra of the samples were obtained with a Lambda 850 spectrophotometer (PerkinElmer) by sandwiching the powder samples between two 3×3 cm quartz slides. Powder X-ray diffraction (XRD) patterns were recorded on a Siemens, Daco-Mp instrument having Cu K α radiation with wavelength of 1.54 Å. The diffractometer was set to 40 kV accelerating voltage and 30 mA, and the data were obtained by setting a wide scan range of 2θ from 20° to 80° with step size of 0.015° and dwell time of 5 s. Transmission electron microscope (TEM) images were obtained with a TOPCON microscope operating at 200 kV on samples prepared on carbon/Formvar-coated Cu grids. The catalytic reactions were analyzed by using an Agilent 6850 GC instrument equipped with an HP-1 column (1% dimethylpolysiloxane, 30 m length, 0.25 mm i.d., and 0.25 μ m film thickness) and a flame ionization detector. The products were further confirmed by a HP 5890 (MSD-5972) GC-MS instrument containing a HP-5 MS 50 m \times 0.200 mm \times 0.33 μ m capillary column. Elemental analyses of the materials were carried out by Robertson Microlit Laboratories (Ledgewood, NJ).

3. RESULTS AND DISCUSSION

Synthesis and Structural Analysis. For the synthesis of SiO_2 @Pd-PAMAM and SiO_2 @Pd core—shell microspheres, first 450 nm silica microspheres, which were synthesized by the Stöber method,³⁸ were etched with KOH (Scheme 1). This produced ~305 nm size nanocurrugated/nanoporous silica microspheres, labeled here as SiO_2 . We have chosen the etched silica microspheres here as support materials for dendrimers or dendrimer-encapsulated catalysts (DECs) because from our previous studies^{39,40} we found that such etched silica microspheres were more conducive to support metallic nanoparticles as well as biomolecules by the virtue of their nanocurrugated surface, nanoporous structure, high surface area, and relatively larger density of surface silanol groups.

To attach G4 PAMAM dendrimers or the DECs onto SiO_2 , first, vinyltriethoxysilane (VTS) was grafted on the surface of the etched silica microspheres. This produced vinyl-functionalized silica (vinylsilica) microspheres. The surface vinyl groups were then converted to epoxides using *m*-chloroperoxybenzoic acid at



Figure 1. FTIR spectra of (a) SiO_2 , (b) vinylsilica, and (c) epoxysilica microspheres and (d) SiO_2 @PAMAM and (e) SiO_2 @Pd-PAMAM core-shell microspheres. See Supporting Figures S1–S4 for enlarged spectra.

room temperature. After centrifugation and washing with anhydrous acetonitrile, epoxysilica microspheres were obtained. On these epoxysilica microspheres, amine-terminated G4 PAMAM dendrimers were covalently anchored through nucleophilic ringopening of the epoxides by the primary amine groups of the G4 PAMAM dendrimers, resulting in SiO2@PAMAM core-shell microspheres. The reaction does not need any catalyst as the silica surface itself or its residual silanol groups served as a mild catalyst for the epoxide ring-opening reaction.⁴² Furthermore, since the terminal primary amine groups of the PAMAM dendrimers are more accessible, they are capable of opening up the epoxides under the reaction conditions we used.^{42a,43} Once one of the few primary amine groups of PAMAM dendrimers anchor onto the epoxysilica microspheres, the other primary amine groups that are not close enough to the epoxy groups remain as they are on the SiO₂@PAMAM core-shell microspheres. These residual primary amine groups were converted to quaternary ammonium ions by stirring the microspheres in dilute HCl solution in order to prevent the amine groups from anchoring Pd(II) ions. This, in turn, prevented the uncontrolled growth of bigger Pd particles on the external surface of PAMAM shell. After this step, Pd(II) ions were anchored by using the residual amido groups within the dendrimer cores. The Pd(II) ions were then reduced into Pd(0) by following Crooks' method.²⁴ This generated Pd nanoparticles (PdNPs) within the cores of the PAMAM shells, resulting in the SiO₂@Pd-PAMAM core-shell microspheres (or SiO₂ supported DEC nanocatalysts).

The materials after each step of syntheses were characterized by FTIR spectroscopy (Figure 1 and Figures S1–S4). The FTIR

Table 1. BET Surface Area Results Obtained from N₂ Gas Adsorption Experiments of the Different SiO₂-Based Microspheres Including SiO₂@Pd-PAMAM Microspheres

sample name	BET surface area, m^2/g
SiO ₂ microspheres	20
etched SiO ₂ microspheres	29
vinylsilica microspheres	25
epoxysilica microspheres	17
SiO2@PAMAM	15
SiO2@Pd-PAMAM	13



Figure 2. TGA of (a) etched silica, SiO₂, (b) vinylsilica, and (c) epoxysilica microspheres and (d) SiO₂@PAMAM core-shell microspheres.

spectrum of SiO₂ microspheres showed a broad O–H stretching peak between 2500 and 3500 cm⁻¹ and a strong Si–O–Si stretching band centered at ~980 cm⁻¹. The spectrum for vinylsilica microspheres showed C–H stretching and vibrational modes corresponding to the vinyl groups at ~3065 and ~1410 cm⁻¹, respectively, and an additional C=C stretching band as a shoulder at ~1610 cm^{-1.44} Upon epoxidation, the stretching peak corresponding to C–H of C(O)–C–H remained at ~3065 cm⁻¹, and a peak corresponding to epoxide appeared at ~909 cm^{-1.45} After the epoxysilica microspheres were reacted with G4 PAMAM dendrimers, a new N–H deformation peak corresponding to amide groups at ~1555 cm⁻¹ appeared.

The N₂ gas adsorption/desorption isotherms for the all the samples are shown in Figure S5. The Brunauer-Emmett-Teller (BET) surface areas of unetched SiO_2 , etched SiO_2 , vinylsilica and epoxysilica microspheres, and SiO2@PAMAM and SiO₂@Pd-PAMAM core-shell microspheres were 20, 29, 25, 17, 15, and 13 $\text{m}^2 \text{g}^{-1}$, respectively (Table 1). Their TGA results (Figure 2 and Table 2) showed a slight weight loss below \sim 120 °C in all the cases, which was attributed to the loss of physisorbed water from the samples. The weight loss from the samples in the range 150-780 °C on the thermogravimetric traces was attributed mainly to the loss of organic groups. In this temperature range, the weight losses from vinylsilica and epoxysilica microspheres and SiO2@PAMAM core-shell microspheres were 5.9, 9.5, and 17.9%, respectively. These weight losses correspond to the loss of vinyl, epoxy, and PAMAMepoxy species, respectively. The trend in increase in wt % loss from vinylsilica to epoxysilica microspheres and then to SiO₂@-PAMAM clearly confirmed the successful anchoring of more

organic groups, including the dendrimers, on the SiO₂ microspheres in subsequent steps of the syntheses. The wt % epoxy and PAMAM groups on the samples were calculated from the difference in the values of these weight losses as shown in Table 2. Further careful analysis of the TGA results (see Supporting Information) indicated that there were \sim 2.25 mmol of epoxides per gram of epoxysilica microspheres. Similar calculation gave \sim 5.90 μ mol of PAMAM per gram of SiO₂@PAMAM core-shell microspheres. Geometrical calculation along with the density of silica of ${\sim}2$ g/cm 3 46 reveals the existence of ${\sim}3.38 \times 10^{13}$ silica microspheres in a gram of \sim 305 nm monodisperse SiO₂ microspheres (Supporting Information). This calculation is reasonable considering the fact that our silica microspheres are monodisperse. When this is combined with the mmol of epoxides and PAMAM per gram of sample, it gives $\sim 4.01 \times 10^7$ epoxides and $\sim 1.05 \times 10^5$ PAMAMs per SiO₂@PAMAM core-shell microsphere. Geometrical calculation (see Supporting Information) is also used to obtain the theoretical surface area of 9.87 m^2 for a gram of \sim 305 nm smooth spherical microspheres. This area is half as much as the experimental BET surface area of $\sim 20 \text{ m}^2/\text{g}$, which was obtained by N2 sorption measurement for the etched \sim 305 nm silica microspheres. The difference between the two surface areas is mainly because the etched microspheres have nanocorrugated and nanoporous surface, while the geometrical calculation is applied to smooth spherical silica microspheres.

The TEM image of the SiO₂@Pd-PAMAM dendrimer coreshell microspheres is shown in Figure 3 and Figures S6–S8. The images clearly show that large numbers of PdNPs are supported on the surface of the SiO₂@Pd-PAMAM core—shell microspheres. The average size of the PdNPs is 1.56 ± 0.67 nm (Figure 3F). The control experiment involving simple impregnation of Pd(II) on SiO₂ microspheres with no PAMAM shells around them also produced PdNPs, or the sample labeled here as SiO₂@Pd. The formation of PdNPs directly on the SiO₂ microspheres is driven by the possible electrostatic interaction between Pd(II) ions and the silanol (Si-OH) groups of the SiO₂ microspheres and the subsequent reduction of the Pd(II) ions into supported PdNPs (Figure S8). However, the number of PdNPs formed in this case was visibly much fewer compared to those on the SiO₂@Pd-PAMAM dendrimer core-shell microspheres, indicating the importance of the PAMAM dendrimers. Furthermore, and most importantly, the PdNPs in SiO₂@Pd appeared to be slightly bigger in size, with sizes up to ${\sim}3.37\pm1.40$ nm. In addition, their particle size distribution appeared more polydispersed (see Figure S8) compared to those in SiO2@Pd-PAMAM dendrimer core-shell microspheres.

The formation of PdNPs in SiO₂@Pd-PAMAM dendrimer core—shell microspheres was confirmed by UV—vis spectroscopy, powder X-ray diffraction (XRD), and elemental analyses. The UV—vis spectrum of SiO₂@Pd-PAMAM core—shell microspheres showed an absorption band at ~229 nm (Figure 4A) corresponding to PdNPs.⁴⁷ Pd(0) nanoparticles, especially very small ones, have no strong plasmon band in the visible region, and they rather have only broad UV—vis absorption bands near UV region with no discernible peak.^{47a,48} The strong and sharp bands in the range of 210–300 nm, particularly at ~210 and ~230 nm, that we have observed could be due to various MLCT bands of Pd²⁺ complexes.⁴⁸ Our UV—vis spectra for SiO₂@Pd-PAMAM micro-spheres, in fact, look very similar to the UV-vis spectrum reported for tannin-stabilized Pd(0) nanoparticles by Huang et al.^{47a}

Furthermore, the wide-angle XRD pattern of the SiO₂@Pd-PAMAM microspheres (Figure 4B) exhibited a broad peak at

sample	composition	% wt loss in the range 200–750 °C	% wt change compared to the proceeding sample	mol of functional groups
SiO ₂	SiO ₂	4.7		
vinylsilica	$SiO_2 - (CH = CH_2)_n$	5.9	1.2	NA ^a
epoxysilica	$SiO_2 - [CH(O)CH_2]_n$	9.5	3.6	2.3 mmol epoxide/g
SiO2@PAMAM	$SiO_2 - [CH(O)CH_2]_{n-m}(PAMAM)_m$	17.9	8.4	5.9 μ mol PAMAM/g

^{*a*} The exact amount of functional group in this case (i.e., vinyl groups) is hard to determine as the weight change from SiO_2 to vinylsilica is not necessarily only due to the addition of vinyl groups but also due to the loss of some of the Si–OH (silanol) groups during grafting of the vinyltriethoxysilane on them.



Figure 3. (A, B) Low magnification and (C) high magnification TEM images of etched SiO₂ microspheres. (D, E) Enlarged TEM images of SiO₂@Pd-PAMAM core-shell microspheres. (F) Size distribution of Pd nanoparticles in SiO₂@Pd-PAMAM core-shell microspheres.



Figure 4. (A) UV-vis spectra of SiO₂@Pd-PAMAM core-shell microspheres. (B) Powder X-ray diffraction pattern of SiO₂@Pd-PAMAM core-shell microspheres.

39.25° that was attributed to the (111) reflection of Pd.⁴⁹ The broad XRD peak is to be expected for such small Pd nanoparticles encapsulated within the dendrimers of the SiO₂@Pd-PAMAM microspheres. The XRD pattern of the Pd nanoparticles in SiO₂@Pd-PAMAM microspheres appears similar to the XRD pattern recently reported for small Pd nanoparticles within mesoporous silica by Jiang and Gao.³⁰

The presence and wt % of Pd in SiO₂@Pd-PAMAM core shell microspheres was further determined by elemental analysis which showed 534 ppm (0.053 wt %) Pd. This was calculated to be 2.5 mmol Pd per gram of SiO_2 @Pd-PAMAM core-shell microspheres.

Catalytic Studies. The catalytic properties of the SiO_2 @Pd-PAMAM microspheres were investigated by using the microspheres as catalyst in hydrogenation reaction of various substrates under 10 bar hydrogen pressure and at room temperature (RT) (Table 3). Control experiments involving attempted hydrogenation reaction without any catalyst or with silica

Entry	Substrate	Products	Time, min	% Conversion	% Selectivity	TOF, h ⁻¹
1 ^b			10 120	9 80	~100 ~100	1812
2			10	~100	~100	24000
3 °			10	~100 40 ^d	~100	10840 4800
4			15	~100	~100	16000
5	\bigcirc	\bigcirc	20	~100	~100	12000
6	$\sim \sim /$	\sim	60	~100	~100	4000
7	o l	ОН	120	~100	~100	2000
8°		O OH	120	95	~100 ^f	2000
9		ОНСНО	180	~100	65 ^g : 35 ^h	1333
10	CI NO2	CI NH2	150	~100	96	1240
11			25	~100	~100	10600
12	O ₂ N	H ₂ N	90	~100 ⁱ 35 ^j 88 ^K	$\sim 100^{-1}$ $\sim 35^{-m}$ $\sim 88^{-n}$	1240

Table 3. Hydrogenation of Various Substrates by SiO₂@Pd-PAMAM Dendrimer Core-Shell Microsphere Catalyst^a

^{*a*} Reaction conditions: substrate: 0.01 mol; methanol: 20 mL; catalyst: 5 mg (0.0053 wt % Pd in the SiO₂@Pd-PAMAM dendrimer core—shell microspheres; 10 bar H₂ pressure; temperature: 20 °C. ^{*b*} Catalyst used was Pd@SiO₂. ^{*c*} Catalyst used was 1% Pd/C. ^{*d*} Third recycle of 1% Pd/C. ^{*c*} Temperature: 50 °C. ^{*f*} 4-Hydroxypentan-2-one. ^{*g*} 1-Phenylethanol. ^{*h*} Phenylacetaldehyde. ^{*i*} In 15 min, all the double bonds were hydrogenated. ^{*i*} In 2.5 h, 35% of the nitro groups were additionally hydrogenated. ^{*k*} In 8 h, 88% of the nitro groups were additionally hydrogenated. ^{*i*} In 15 min, 100% selectively to 4-nitroethylbenzene product was obtained. ^{*m*} In 2.5 h, 35% of 4-ethylaniline and 65% 4-nitroethylbenzene were obtained. ^{*n*} In 8 h, 88% 4-ethylaniline and 12% 4-nitroethylbenzene were obtained. See Figure S10 also for GS-MS spectra.

microspheres containing no Pd (SiO₂ and SiO₂@PAMAM) gave almost no reaction or no hydrogenation product. However, the SiO₂@Pd-PAMAM microspheres catalyzed the hydrogenation reactions of various substrates well, giving the corresponding hydrogenated products, as confirmed by GC and GC-MS (Tables 3 and 4 and Figure S9). For instance, the hydrogenation of styrene in the presence of SiO2@Pd-PAMAM core-shell microspheres resulted in ethylbenzene with $\sim 100\%$ conversion in 10 min at RT and with a high net rate of 23 880 h^{-1} . This showed that the catalytic activity of the SiO2@Pd-PAMAM core-shell microspheres was even higher than that of the very active shaped Pd nanoparticle catalysts in nanoporous silica that we have recently reported.⁵⁰ The catalytic efficiency of the SiO₂@Pd-PAMAM core-shell microspheres was also compared with commercially available 1 wt % Pd/C catalyst. When the latter was used as catalysts for hydrogenation of styrene under the

same conditions, ~100% conversion in 10 min was obtained; however, the TOF of the Pd/C catalyzed reaction was found to be about half as much as that of SiO₂@Pd-PAMAM core—shell microspheres. Whereas the 1 wt % Pd/C for this reaction yielded a net rate of 10 260 h⁻¹ (Table 3, entry 3), the SiO₂@Pd-PAMAM core—shell microspheres gave a net rate of 24 000 h⁻¹. Furthermore, the SiO₂@Pd-PAMAM core—shell microspheres were found to be highly recyclable at least five times with almost no change in their catalytic property giving similar net rate, where as the 1 wt % Pd/C lost its activity, significantly giving a net rate of 4800 h⁻¹ after the third recycle (see Figure 5).

Another control experiment involving a catalytic reaction with a catalyst prepared by physisorption of premade Pd-PAMAM nanoparticles (or DECs) on the surface of SiO_2 microspheres was performed. This catalyst gave significantly lower catalytic activity in catalytic hydrogenation of styrene, and most importantly, it

Table 4. Results for the Recycle Catalytic Reactions for SiO_2 @Pd-PAMAM Core-Shell Microsphere Catalysts for the Hydrogenation of Styrene^{*a*}

entry	recycle no.	t, min	% conv	% selectivity b	net rate, $h^{-1 c}$
1	0	7	76.5	~ 100	23 880
2	1	7	76.5	~ 100	23 880
3	2	7	76.2	~ 100	23 810
4	3	7	76.2	~ 100	23 810
5	4	7	76.2	~ 100	23 810
6	5	7	76.0	~ 100	23 780

^a Reaction conditions: styrene: 0.01 mol; methanol: 20 mL; catalyst: 5 mg (0.0053 wt % Pd in the SiO₂@Pd-PAMAM core-shell microspheres); 10 bar H₂ pressure; temperature: 20 °C; reaction time: 10 min. Selectivity to ethylbenzene product. ^c The net rate was calculated by dividing the mmol of product formed in 7 min by mmol of catalyst used in the reaction and then normalizing all the results for 1 h for comparison purposes. It is worth mentioning that the hydrogenation reaction of styrene with our catalyst is extremely fast, getting almost into completion within 10 min of reaction time. The reaction was monitored by measuring the drop in H2 pressure in the reactor due to the hydrogenation reaction as precisely as possible using a pressure gauge that comes with the Parr reactor. Furthermore, the reaction times were collected with stop watches as precisely as possible. Moreover, because of the unavoidable slight loss of catalyst during recovery, the amount of reactant used in the next cycle was scaled down accordingly in order to maintain the reactant/catalyst ratio as constant as possible in all of the five cycles for comparison purposes.

resulted in severe leaching of the DECs into the reaction solution. These microspheres were also found to contain less Pd-PAMAM per silica microsphere. This clearly indicates the advantage of covalent attachment of the Pd-PAMAM DECs onto the SiO_2 microspheres in order to increase the stability of the DECs.

To study the scope of the catalytic activity of the SiO₂@Pd-PAMAM microspheres, the catalytic hydrogenation reactions of substrates other than styrene were explored (Table 3). For instance, the SiO₂@Pd-PAMAM core-shell microspheres catalyzed the hydrogenation of phenylacetylene to ethylbenzene. The hydrogenation of phenylacetylene was found to be slightly slower than that of styrene (Table 3, entry 4). This was, however, to be expected considering the fact that the hydrogenation of phenylacetylene to ethylbenzene goes through two hydrogenation steps, i.e., phenylacetylene to styrene and then styrene to ethylbenzene. The catalyst, nevertheless, still exhibited high catalytic activity and TOF even for such two-step hydrogenation reaction. The hydrogenation of another reactant, cyclohexene, took place with almost \sim 100% conversion in 20 min in the presence of the SiO₂@Pd-PAMAM core-shell microspheres under the same reaction condition (Table 3, entry 5). In addition, the SiO₂(a)Pd-PAMAM core-shell microspheres catalyzed n-hexene with \sim 100% conversion in 60 min (Table 3, entry 6). More interestingly, although ketones undergo hydrogenation rather relatively slowly,⁵¹ the SiO₂@Pd-PAMAM core-shell microspheres catalyzed the hydrogenation of acetone and acetylacetone efficiently and with high TOF. The catalytic hydrogenation of acetone with SiO₂@Pd-PAMAM core-shell microspheres gave a sole product, isopropanol, with \sim 100% conversion in 2 h at 50 °C, whereas the catalytic hydrogenation acetylacetonate gave 4-hydroxypentan-2one with 95% conversion in 2 h (Table 3, entries 7 and 8).

The hydrogenation of styrene oxide into 1-phenylethanol—an important compound in the fragrance industry⁵²—was also

demonstrated using the SiO₂@Pd-PAMAM core—shell microspheres as catalyst. The reaction gave ~100% conversion in 3 h, yielding 65% of 1-phenylethanol and 35% of phenylacetaldehyde products (Table 3, entry 9). The catalytic activity of the SiO₂@Pd-PAMAM microspheres was also tested with 4-chloronitrobenzene—a less reactive compound to undergo hydrogenation.⁵³ The SiO₂@Pd-PAMAM core—shell microspheres catalyzed the reaction with 100% conversion and 96% selectivity to 4-chloroaniline product in 2.5 h and at a slightly elevated temperature of 50 °C (Table 3, entry 10). The SiO₂@Pd-PAMAM core—shell microspheres were also found to catalyze the hydrogenation of *trans*-stilbene to generate 1,2-diphenylethane successfully with ~100% conversion in 25 min (Table 3, entry 11).

The SiO₂@Pd-PAMAM core—shell microspheres' selectivity to catalytically hydrogenate different functional groups was tested using 4-nitrostyrene, which has a nitro group and a vinyl group that can undergo hydrogenation (Table 3, entry 12). In the initial period of the reaction, only the vinyl groups underwent catalytic hydrogenation in the presence of the SiO₂@Pd-PA-MAM core—shell microspheres almost completely in ~15 min. Then, the nitro groups followed and underwent hydrogenation into amine groups almost completely in ~2.5 h.

The reusability of SiO2@Pd-PAMAM core-shell microspheres as catalyst was tested using styrene hydrogenation as a model reaction (Table 4). This was performed by collecting the SiO₂@Pd-PAMAM core-shell microspheres from the preceding reaction via simple centrifugation and then reusing them as catalyst in the next cycle. The SiO₂@Pd-PAMAM core-shell microspheres were proven to be effectively recyclable catalysts at least in five cycles with barely losing their catalytic activities. Their TOF remained between 23 780 and 23 880 h^{-1} after five cycles. On the other hand, the SiO2@Pd microspheres (control sample), which contained no PAMAM on their shells, also catalyzed the hydrogenation of styrene to ethylbenzene with similar catalytic efficiency, giving 98% conversion in 10 min and 23 750 h^{-1} TOF in the first cycle. However, they quickly lost their catalytic activities after recycling, giving only 61, 54, and 40% conversions and 14 783, 13 086, and 9693 h^{-1} TOFs, respectively, after the first, second and third cycles (Table 5). These TOF values were significantly lower than the corresponding values obtained for the SiO₂@Pd-PAMAM core-shell microspheres.

Furthermore, leaching tests for the SiO₂@Pd-PAMAM core shell microspheres in the catalytic reactions were conducted. The catalytic reaction of the supernatant, after separating the SiO₂@Pd-PAMAM core—shell microspheres from the reaction mixture, gave only 1% styrene conversion in an additional 10 min, indicating the "true" heterogeneous catalytic nature of the SiO₂@Pd-PAMAM core—shell microspheres. This result was corroborated by ICP-OES analysis of palladium in the reaction mixture after the first, third, and fifth reaction cycles, which showed <1 ppm palladium in the solutions.

It is worth mentioning that under the experimental conditions we performed the hydrogenation reaction using the SiO₂@Pd-PAMAM microspheres as catalysts, the arene groups of styrene and the substrates did not undergo hydrogenation, while the vinyl and nitro functional groups did. It is not clear whether this is because the arene groups are too big to penetrate through DENs and reach to the Pd nanoparticles, or the arene groups do not undergo catalysis with our SiO₂@Pd-PAMAM microsphere catalysts under the conditions we employed. Whatever the case might be, this difference in reactivity between the vinyl and arene groups can be taken advantage of and potentially utilized to



Figure 5. (A) Comparative graph for % conversion of styrene in 10 min versus recycle time of $SiO_2@Pd$ -PAMAM core—shell catalysts and commercial Pd/C (1%) catalyst. (B) Catalytic efficiency of recycled Pd/C catalyst showing significant catalytic activity loss after recycling. A similar graph for $SiO_2@Pd$ -PAMAM core—shell catalysts was difficult to plot because of the materials' very high catalytic activities and the fast H₂ consumption by the reaction.

Table 5. Catalytic Activities of SiO_2 @Pd Microspheres in Multiple Cycles of Catalytic Test^{*a*}

entry	times recycled	% conv	% selectivity ^b	net rate, h^{-1} c
1	0	98	~ 100	23 750
2	1	61	~ 100	14 783
3	2	54	~ 100	13 086
4	3	40	~ 100	9 693
5	4	23	~ 100	5 573
6	5	19	~ 100	4 604

^{*a*} Reaction conditions: substrate: 0.01 mol; methanol: 20 mL; catalyst: 5 mg (0.05 wt % Pd in the SiO₂@Pd microspheres; 10 bar H₂ pressure; temperature: 20 °C; and reaction time: 10 min. ^{*b*} Selectivity to ethylbenzene product. ^{*c*} The net rate was calculated by dividing the mmol of product formed in the specified time by mmol of catalyst used in the reaction and then normalizing all the results for 1 h for comparison purposes.

perform selective catalysis of only vinyl or nitro groups in the presence of arene groups. A similar idea of size selective catalysis has actually been successfully demonstrated by an elegant work of Crooks and co-workers,⁵⁴ who showed that the rational design of the periphery of dendrimers would allow preferential size-dependent selective hydrogenation of smaller α -allylic alcohols.

It is also worth noting that the conditions we employed for hydrogenation reaction, 10 atm H₂ pressure, is relatively, but not surprisingly, high. There are literature reports on hydrogenation reactions using lower H₂ pressure, for instance 100 Torr of H₂ (~0.13 atm).⁵⁵ However, in many of these cases, the reactions are often done under vacuum and for gas phase hydrogenation of substances such as ethylene. Furthermore, in most of these cases, although the H₂ pressure is set to be low, the other gases such as ethylene or argon make up the overall pressure. For instance, in the report by Molero et al.,^{55a} the authors used ethylene pressures between 50 and 300 Torr and H₂ pressures from 45 to 600 Torr at 300 and 475 K to do ethylene hydrogetation in gas phase. In another example reported by Cremer et al.,^{55b} the authors used near 1 atm of total pressure of ethylene and H₂ at 295 K to perform ethylene hydrogenation. The authors further reported that at such intermediate pressures of 100 Torr of H₂ gas the richest surface chemistry with infrared-visible sum frequency generation (SFG), which was used to monitor the surface vibrational spectrum *in situ* during ethylene hydrogenation on Pt(111) at 295 K, was obtained. Thus, these low pressures are chosen mainly to perform experiments of these types in ultrahigh vacuum (UHV) systems to probe reaction mechanisms.

On the other hand, experiments in our case using very low H_2 pressure are not very feasible because the alkene is in liquid form and the reaction mixture is in solution phase. In hydrogenation of alkenes in liquid phase, the hydrogen pressures are often set to a much higher pressures than 100 Torr to get reasonable yield/ TOF.⁵⁶ For instance, in the work by Oyamada et al.,^{56a} the authors used 0.15 MPa or 1.48 atm (a much higher pressure than 100 Torr) for hydrogenation of various organic compounds. They obtained (the highest) TON of 2700 in 1.5 h (or a TOF value of 1800 h^{-1}), which was much lower than the one obtained in our case, which was $24\,000$ h⁻¹; however, the pressure used in our case was high, i.e., 9.8 atm. In the work by Xu et al.,^{56b} the authors used 1.5 MPa or 14.8 atm H₂ pressure for hydrogenation of various nitroaromatices in solution phase using Pt nanoparticles. Although the H₂ pressure used in their case was actually higher than the one used in our case, the conversion of the nitro groups in their catalytic reactions also reached \sim 90–100% only in 1–10 h.

To further evaluate the catalytic activities of the SiO₂@Pd-PAMAM core—shell microspheres, we also conducted the hydrogenation of styrene under lower pressure (1 atm or 1.01 barr) of H_2 in the presence of the SiO₂@Pd-PAMAM core—shell microspheres. We obtained only 7% conversion in 4.5 min. Soon after this, the H_2 pressure dropped to 0.27 atm and the reaction barely continued afterwards. When setting the pressure in the reaction mixture to 1 atm again, the reaction gave 6% more reactant conversion, followed by a significant drop in the H_2 pressure as well as in the reaction rate.

In addition, we compared the net rate of SiO₂@Pd-PAMAM core-shell microsphere catalyst (i.e., \sim 24 000 h⁻¹) with values

reported for similar catalysts in the literature. For instance, compared with the catalytic activity of nanoporous silica encapsulated Pd nanoparticle catalysts that we have recently reported⁵⁰ and that gave net rate of 2800-5400 h⁻¹, the catalytic activity of the SiO₂@Pd-PAMAM core-shell microspheres was higher. Furthermore, compared with the highest TOF value of 4.37 s^{-1} for Pd catalysts reported by Mastalir et al.,⁵⁷ the one we obtained for SiO₂@Pd-PAMAM core-shell microspheres (~24 000 h⁻¹) was again higher. In the work by Mekasuwandumrong,⁵⁸ typical TOF values ranged from 4.3 to 66.2 s^{-1} (which were 258 to 3972 h^{-1} when converted into h^{-1} for comparison purposes) for different silica-supported palladium nanomaterials were reported. This result also showed that the catalytic activity of the SiO₂@Pd-PAMAM microspheres was higher than that of these Pd catalysts reported by Mekasuwandumrong.⁵⁸ In the work by Jackson et al.,⁵⁹ ~100% conversion of alkene in much longer reaction time of 40 min, but under much lower reaction pressure than those used in our case, was reported. In the work by Nijhuis et al.,⁶⁰ a catalyst with 2% Pd on Davisil 643 was reported to catalyze hydrogenation at 1 bar pressure of alkyne into alkene almost completely in 10 min, with further conversion of the resulting alkene into alkane after \sim 20 min more. Comparing the above results, we notice that our SiO2@Pd-PAMAM microsphere catalysts perform well, if not better than some of them. In fact, only in case of Pt nanoparticles,⁶¹ we find a much higher net rate (i.e., 65 041 h⁻¹ for hydrogenation of nitrobenzene) than those obtained in our case. Nonetheless, since the catalysts and reaction conditions in each system, including ours, are different, it is difficult to make a full scale comparison or conclusion on the relative efficiency of our SiO2@Pd-PAMAM microsphere catalysts with respect to others.

4. CONCLUSIONS

In summary, we have developed a synthetic route to novel SiO₂@Pd-PAMAM core-shell microspheres or heterogeneous nanocatalysts. Their synthesis involved supporting PAMAM dendrimers covalently onto etched silica microspheres and then encapsulating small and monodisperse palladium nanoparticles (PdNPs) within the supported PAMAM dendrimers. The resulting SiO2@Pd-PAMAM core-shell microspheres exhibited highly efficient and recyclable catalytic activities in catalytic hydrogenation of various substrates and functional groups. Furthermore, because of their silica microsphere supports, their coreshell structures and their ultrasmall PdNPs, the SiO₂@Pd-PA-MAM core-shell microspheres showed better catalytic activities and recyclability with no loss of their catalytic activities compared with their corresponding control samples, including SiO₂@Pd coreshell microspheres that contain no dendrimers and a commercially available Pd/C (1 wt %) catalyst.

ASSOCIATED CONTENT

§ Supporting Information. FTIR spectra, transmission electron micrographs, N_2 gas adsorption isotherms, and GC-MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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