Journal of
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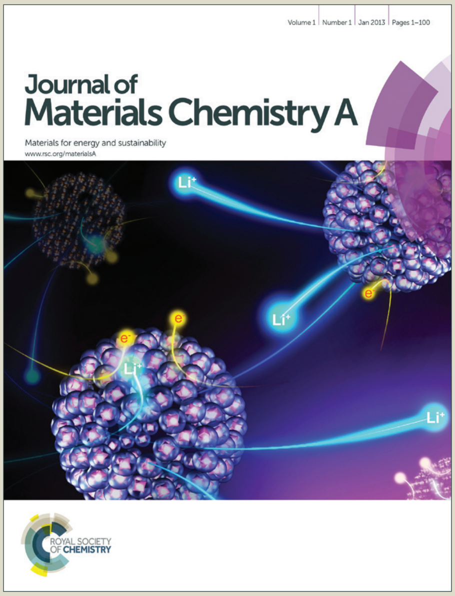

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Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Magnetically Recyclable Core-Shell Nanocatalysts for Efficient Heterogeneous Oxidation of Alcohols†

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We describe on the designed fabrication of magnetically recyclable core-shell Pd nanocatalysts for the efficient oxidation of alcohols under base-free reaction conditions in water. The Pd NPs that are half-partitioned in the polymer matrix can provide not only high catalytic activity but also stabilization of the nanocatalysts under harsh reaction conditions. Furthermore the magnetic separation provides a convenient method for removing and recycling the active Pd nanocatalysts from the reaction mixture. The designed nanocatalysts can be readily synthesized in a large scale and were able to be reused for five consecutive cycles of the oxidation of cycloheptanol. The nanocatalysts present high catalytic activity in other types of catalytic reactions involving Pd NPs such as Suzuki cross-coupling and reduction of nitroarenes.

Introduction

The oxidation of alcohols to aldehydes or ketones is a fundamental chemical transformation for the production of a large variety of important intermediates and fine chemical products.[1] Among the transition metals, palladium shows very promising catalytic properties in the form of complexes, heterogeneous metal catalysts or nanoparticles (NPs).[2] Catalytic NPs present a high surface-to-volume ratio and therefore possess promising applications for catalytic reactions. However, most Pd NP catalysts have been somewhat limited in use due to the challenges in separating and reusing the expensive catalysts. Consequently, typical industrial heterogeneous catalysts are composed of supported metal NPs owing to their advantages of recovering and reusing of the catalysts. Furthermore, it has been shown that NP-based catalysts (nanocatalysts) generally do not retain high catalytic reactivity under corrosive reaction conditions without a sturdy support.[3] Nanocatalysts without any support are generally unstable and structural deformation occurs after a single use in harsh catalytic reactions.[4]

Although significant progress has been achieved to improve the catalytic activity, selectivity and substrate breadth, there are still major problems with nanocatalysts. Primarily agglomeration of palladium NPs and instability under destructive reaction conditions cause rapid catalyst deactivation leading to limited use of nanocatalysts in practical applications.[5] Therefore, most alcohol oxidations are carried out under high oxygen pressure using toxic organic solvents.[6] In the presence of active oxidants, unstable supports or surfactants often decompose and cause deformation of nanocatalysts.[7] As a result, the size, shape, composition and reactivity of nanocatalysts change during such reactions.[8] By using stabilized nanocatalysts under mild oxidation conditions (e.g. H_2O_2) in water, these problems can be overcome yielding a less expensive, safer and more environmentally benign oxidation protocol. Thus it is an important issue to develop economical and scalable approaches for preparing highly active, recyclable and stable nanocatalysts to perform green chemical processes and reduce the manufacturing cost.[9] To solve these problems various techniques have been developed.[10] Recently, hybrid nanocomposites with magnetic core-shell nanostructures increasingly attracted attention in heterogeneous catalytic reactions.[11] However, while supporting the nanocatalysts can increase their stability, it also decreases their reactivity.[12] To circumvent these drawbacks, we herein fabricated Pd NPs robustly fixed on a polymer layer of magnetic silica core-shell nanospheres for magnetically separable and recyclable catalysts for heterogeneous alcohol oxidation. The Pd NPs that are half-partitioned in the polymer matrix can provide not only high catalytic activity but also stabilization of the nanocatalysts under harsh reaction conditions. The designed nanoccatalysts present

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† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

excellent catalytic activities for oxidation of alcohols under base-free reaction conditions in water. The nanocatalysts could also find applications in other types of nanocatalyzed reactions involving Pd NPs such as Suzuki cross-coupling and reduction of nitro aromatics. Furthermore the magnetic separation provides a convenient method for removing and recycling the active Pd nanocatalysts from the reaction mixture.

Experimental

Materials and characterizations

Water was deionized by a Nano Pure System (Barnsted). The chemicals used in this work were purchased at the highest possible grade from Aldrich, Samchun, and Gelest. Transmission electron microscope (TEM) images were obtained using JEOL JEM 1010 at 80 kV and JEOL EM-2010 microscope at an acceleration voltage of 200 kV. High resolution TEM (HRTEM) images were obtained using a JEOL JEM-3010 microscope equipped with energy-dispersive X-ray spectroscopy (EDX) detector. Scanning transmission electron microscopy (STEM), High resolution STEM (HRSTEM) and annular dark-field imaging (HAADF) images were acquired using a JEOL JEM-2100F. Field emission scanning electron microscopy (FESEM) images were obtained by a SUPRA 55VP Carl Zeiss instrument. Focused ion beam field-emission scanning electronic microscopy (FIB-FESEM) images were obtained by a Carl Zeiss Auriga. Size of nanocatalysts was characterized by the dynamic light scattering (DLS) measurements (Zetasizer Malvern Instruments). Small-angle X-ray scattering (SAXS) analyses were obtained using a Bruker AXS, DE/D8 Discover with GADDS instrument. X-ray photoelectron spectroscopy (XPS) was collected using Al Kα source (Sigma probe, VG Scientifics). Powder X-ray diffraction (XRD) was obtained with a Rigaku D/Max-3C diffractometer, equipped with a rotating anode and a Cu Kα radiation source (λ= 0.15418 nm). High resolution powder X-ray diffraction (HRXRD) was obtained with a Bruker D8 Advance instrument. X-ray fluorescence (XRF) spectrometry was recorded by a Bruker AXS S4 pioneer. Thermogravimetric analysis (TGA) result was obtained by a TA Instruments Q-5000 IR USA. The IR spectra were recorded with an ATR-IR Perkin Elmer spectrometer frontier. Inductivity coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu ICPS-7500 Japan) was used for the elemental analysis. The products of the catalytic reactions were analyzed by gas chromatography mass spectrometers (GC-MS) using an Agilent Technologies 5975C VLSMD with triple-axis detector and a Hewlett Packard 5973 mass selective detector GC-MS.

Synthesis of Fe_3O_4 NPs

In a typical synthesis of iron oleate complex, 10.8 g of iron chloride ($FeCl_3 \cdot 6H_2O$, 40 mmol) and 36.5 g of sodium oleate (120 mmol) was dissolved in a mixture solvent composed of 80 ml ethanol, 60 ml distilled water and 140 ml hexane. The resulting solution was heated to 70 °C and kept at that temperature for 4 h. Then, the upper organic layer containing the iron-oleate complex was washed three times with distilled water in a separatory funnel. After washing, hexane was evaporated, resulting in iron-oleate complex in a waxy solid form. 36 g (40 mmol) of the synthesized iron-oleate complex and 5.7 g of oleic acid (20 mmol) were dissolved in 200 g of 1-octadecene at room temperature. The reaction mixture was heated to 300 °C with a constant heating rate of 3.3 °C min^{-1}, and kept at that temperature for 1 h. The resulting solution containing the nanocrystals was cooled to room temperature, and 500 ml of ethanol was added to the solution to precipitate the nanocrystals. The nanocrystals were separated by centrifugation and dispersed in cyclohexane.

Synthesis of silica-coated Fe_3O_4 NPs and *N*-(3-trimethoxysilylpropyl)-pyrrole functionalized core-shell NPs

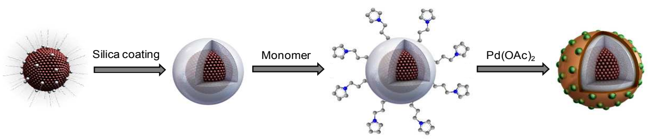
0.5 g of synthesized Fe_3O_4 NPs was dispersed in 100 ml cyclohexane containing 7 g igepal® CO-520. To this solution, 2 ml aqueous ammonia was directly added. Tetraethoxysilane (TEOS 2 ml) was then rapidly added and the solution was vigorously stirred at room temperature for 7 h to obtain silica coated iron oxide NPs. After ageing, the pyrrole functionalized silica shell was formed by the addition *N*-(3-Trimethoxysilylpropyl)-pyrrole (0.4 ml) for 3 h. The product was isolated by centrifugation, washed with ethanol and dispersed in 50 ml ethanol.

Synthesis of the magnetically recyclable core-shell Pd nanocatalysts

While vigorous stirring, 300 mg palladium(II) acetate dissolved in chloroform/ethanol was added dropwise to the functionalized core-shell NPs, and the mixture was stirred for 3 h at room temperature to produce magnetically recyclable nanocatalysts. The color of the mixture changes from light brown to deep black indicating the reduction of the $Pd(OAc)_2$ by pyrrole moiety. The product was washed several times with chloroform/ethanol and dried in vacuo. The palladium loading of the product was measured by ICP-AES.

Results and Discussion

The overall synthetic procedure is shown in Scheme 1. Magnetic NPs were synthesized by modifying a previously reported method.[13] Uniform 20 nm-sized iron oxide NPs dispersed in cyclohexane were coated with a thin layer of silica allowing the surface of the core-shell nanocomposite to be easily functionalized by *N*-(3-trimethoxysilylpropyl)-pyrrole. Finally Pd NPs were embedded on the surface of core-shell nanospheres to produce highly active Pd nanoctalysts. The color of the mixture changed from light brown to deep black indicating the reduction of $Pd(OAc)_2$ by the pyrrole moiety. The thin polymer layer of the designed Pd nanocatalysts is prepared through a redox reaction between pyrrole and $Pd(OAc)_2$. Pyrrole monomers can be chemically polymerized using palladium(II) acetate as an oxidizing agent. This procedure provides *in situ* chemical reduction of palladium ions during pyrrole oxidation so that it inserts uniform Pd NPs in the polymer matrix. The outer polymer shell supports the Pd nanocatalysts from sintering and maximizes the interaction and reactivity of precious catalysts while the impermeable silica layer isolates the core magnetic NPs and prevents the possibility of side reactions during the reaction. In addition, any synergistic effect of the catalytic NPs and the support can be promoted when such interfaces are important in catalytic performances.



Scheme 1. Synthetic procedure for the magnetically recyclable core-shell nanocatalysts.

We synthesized and investigated the composition of the polypyrrole nanocomposite through a direct redox reaction between *N*-(3-trimethoxysilylpropyl)-pyrrole and a Pd precursor as an oxidizing agent. TEM and HRTEM images of the polymer nanocomposite indicate the formation of a polymeric structure and Pd NPs. As shown in Fig. S1 (ESI†) the Pd NPs are relatively uniform with an average size of 3 nm which are incorporated into the polymer matrix. The composition of polymer and presence of Pd NPs in the synthesized nanocomposite were verified by XPS analysis (Fig. S2, ESI†). The TEM images of the magnetic iron oxide NPs showed they were uniform spheres with a size of 20 nm (Fig. 1a). TEM and HRTEM images of silica coated Fe_3O_4 NPs showed uniform core-shell nanostructures with a thickness of ~ 15 nm (Fig. 1b). TEM and HRTEM images also revealed relatively uniform Pd NPs ~ 3 nm in diameter incorporated discretely in a thin polymer layer deposited on magnetic silica core-shell nanospheres (Fig. 1c, d). FESEM images show the magnetically recyclable Pd nanocatalysts exhibit a rough surface due to the accommodation of the Pd NPs in the polymer layer whereas the dense silica-coated magnetic NPs appear to have a smooth surface (Fig. 1e, f). Fig. 2 shows a detailed structural characterization of the designed Pd nanocatalysts obtained by various electron microscopic techniques.

STEM and HRSTEM images confirm a homogeneously assembled nanostructure with Pd NPs implanted in the polymer shell (Fig. 2a, c).

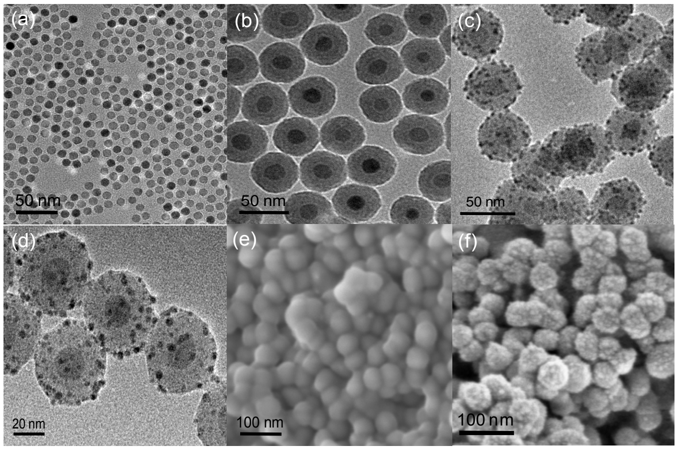


Fig. 1 TEM images of Fe_3O_4 NPs (a), silica coated Fe_3O_4 NPs (b), and the magnetically recyclable Pd nanocatalysts (c). HRTEM image of the magnetically recyclable Pd nanocatalysts (d). FESEM images of silica coated Fe_3O_4 NPs (e), and the magnetically recyclable Pd nanocatalysts (f).

HAADF image revealed the distinct contrast of Pd NPs, silica shell and magnetic NP core (Fig. 2b). The overall size of the nanospheres was observed to be ~ 50 nm by HRTEM which was in good agreement with the DLS data (Fig. 3a). The images obtained by HRTEM (Fig. S4, ESI†) and milling of the Pd nanocatalysts using a FESEM instrument equipped with FIB (Fig. 3d–f) of the Pd nanocatalysts indicated a narrow shell (~ 2 nm) of polymer surrounded the exterior of silica layer in magnified image. In addition, the ATR-IR spectrum of the polypyrrole layer on the silica shell exhibited strong characteristic vibration peaks of ring, C─N and C─H stretching at 1550, 1415, and 930 cm^{-1}, respectively (Fig. 3b). SAXS measurements were carried out to verify the structure of Pd NPs on the designed nanocatalysts in comparison to commercially available Pd/C catalyst (Fig. 3c). The existence of Pd NPs (Fig. 3d) and other components (Fig. S3, ESI†) on the designed nanocatalysts was also confirmed by XPS analysis. EDX (Fig. 3g) and XRF spectrometry (Fig. S5, ESI†) data ascertained the composition of the magnetically retrievable nanocatalysts. The EDX line profile of Pd NPs shown in Fig. 3e was obtained along with the magnified HRSTEM image. The presence of components in the silica coated magnetic NPs was further verified by XPS analysis (Fig. S6, ESI†). The HRXRD pattern revealed that the nanocatalysts are composed of Fe_3O_4 and Pd NPs (Fig. 3f). The magnetic behavior of the nanocatalysts was investigated using a superconducting quantum interference device (SQUID) magnetometer. The field dependent magnetization curve at 300 K reveals superparamagnetic property (Fig. S7, ESI†), which is an advantageous characteristic of the designed nanocatalysts for magnetic separation and subsequent redispersion for efficient recycling.

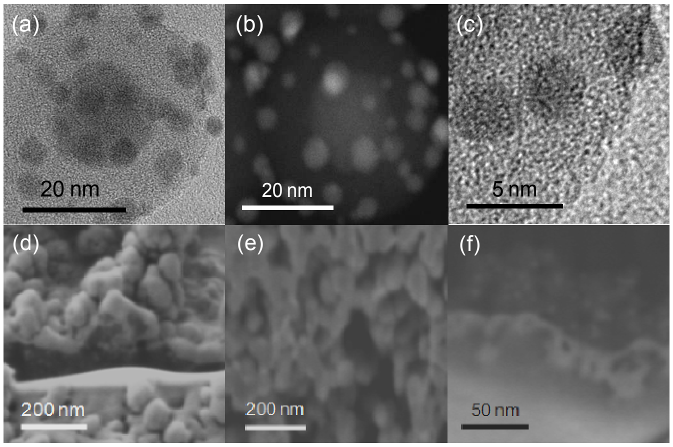


Fig. 2 STEM (a), HAADF (b), HRSTEM (c), and FIB (d–f) images of magnetically recyclable nanocatalysts.

CHN elemental analysis provided the composition of C (9.3%) and N (3.8%) (Table S1, ESI†). The results from thermal gravimetric analysis (TGA) clearly identified stepwise decomposition of different components in the synthesized nanocatalysts (Fig. S8, ESI†). The potential and efficiency of the designed nanocatalysts as active and stable catalysts was investigated in the oxidation of alcohols in water. The Pd loading on the designed nanocatalysts, measured by ICP-AES, was found to be ~ 3.2 wt%. As shown in Table 1, the Pd nanocatalysts showed high catalytic activity for oxidation of various primary and secondary alcohols under base-free reaction conditions to afford the corresponding aldehyde or ketone. It is noteworthy that the Pd nanocatalysts were also very effective for the oxidation of nonactivated alkanols. For example, the oxidation of cyclooctanol took place in water under the optimized reaction conditions to produce cyclooctanone in 95% yield (Table 1, entry 5). In addition, the reactions were very clean with no observable byproduct. In particular, we were efficiently able to trap the product at the corresponding carbonyl stage rather than over-oxidizing to the carboxylic acids. To better clarify the role of the designed polymer shell and well-defined catalytic NPs encrusted on the core-shell nanostructures in our protocol, we performed several control experiments using the oxidation of cycloheptanol as a model reaction. The catalytic activities are summarized in Table 2. We first carried out the oxidation of cycloheptanol without any catalyst using H_2O_2 as oxidant and H_2O as solvent. Interestingly, we found the reaction could produce a low yield (25%) of cyclooctanone after 12 h at 80 °C. Then we investigated the oxidation of cycloheptanol under homogeneous catalytic conditions using K_2PdCl_4. This catalyst did not show any activity under these oxidative conditions. To study the heterogeneous systems, we examined the catalytic reactivity of unsupported 5 nm Pd NPs (Fig. S9, ESI†) prepared by modifying a previously reported method.[14]

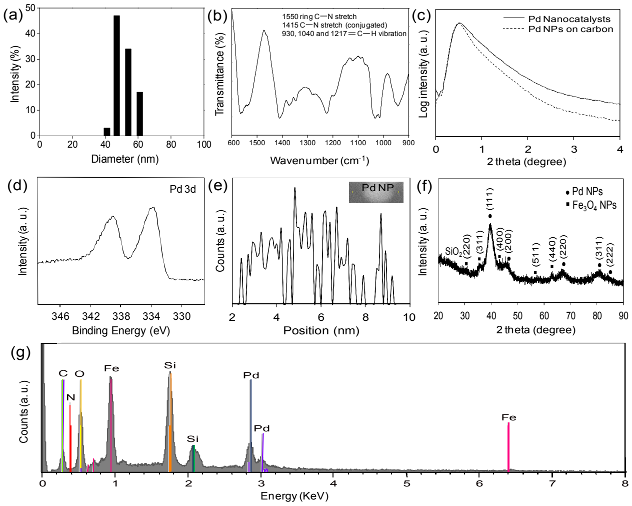
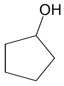
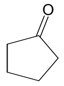
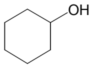
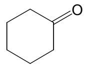
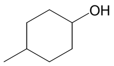
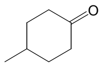
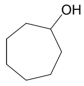
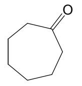
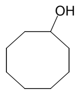
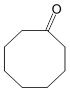
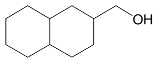
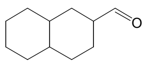
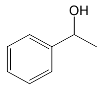
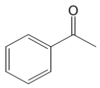
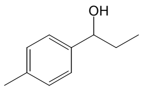
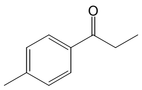
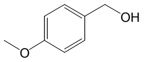
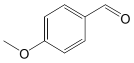
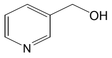
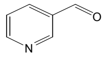


Fig. 3 DLS diagram (a), ATR-IR (b), SAXS (c), XPS (d), line EDX profile (d), HRXRD (f), and EDX (g) spectra of the magnetically recyclable Pd nanocatalysts.

The NPs aggregated immediately after adding H_2O_2, resulting in very low yield of product. When we tested the catalytic performance of the commercially available Pd/C and Pd/charcoal catalysts with a size distribution of 5 to 25 nm (Fig. S10a, b ESI†) for the oxidation of cycloheptanol under the identical reaction conditions, better yield of the product (53% and 48%, respectively) could be observed after 12 h. From this experiment we see the NP catalysts stabilized on a sturdy support provide a higher product yield. Therefore, we designed and synthesized nanostructures without a polymer shell in which Pd NPs were loaded by $NaBH_4$ reduction on the silica layer of the core-shell NPs. TEM studies show that aggregation of Pd NPs is inevitable if they are directly loaded on the silica surface (Fig. S11, ESI†). We conducted the oxidation reaction under the same reaction conditions as before, but using the dense silica shell supported polydisperse Pd NP catalyst. The disordered catalysts provided very low reactivity for oxidation of alcohols under oxidative reaction conditions. Finally we screened the oxidation of cycloheptanol catalyzed by Pd NPs loaded on different solid supports. In these cases, the solid catalysts were prepared by reducing Pd precursor by $NaBH_4$ on various supports.[15] Polydispersed Pd NPs supported on carbon (Fig. S12, ESI†), mesoporous carbon (Fig. S13, ESI†), SBA-15 mesoporous silica (Fig. S14, ESI†), and hydroxyapatite (Fig. S15, ESI†) provided poor to moderate catalytic activities for oxidation of cycloheptanol (Table 2), but showed a rapid agglomeration under these oxidative reaction conditions. In the aforementioned experiments, the significant deactivation of the disordered NP catalysts after adding H_2O_2 and a color change to dark black is presumably a consequence of the formation of palladium black.[16] The unprotected Pd NPs on the surface of rigid supports might be poisoned under oxidative reaction conditions and the agglomeration can be promoted by water.[17]

Table 1. Heterogeneous oxidation of alcohols catalyzed by the magnetically retrievable Pd nanocatalysts.[a]

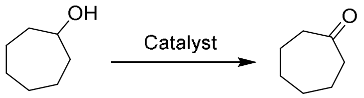
Entry	Alcohol	Product	Yield (%)[b]
1			83
2			70
3			82
4			99
5			95
6			99
7			99
8			40
9			45
10			99

[a] Reaction conditions: alcohol (0.25 mmol), Pd nanocatalysts (1 mol%), 80 °C, H_2O_2 30% (0.75 mmol), H_2O (2.5 ml), 12 h. [b] Yields were determined by GC-MS analysis using internal standard (decane).

In addition, the reuse of the explained catalysts is very challenging due to requirement of filtration, centrifugation and tedious work-up processes. When we compared the reactivity and stability of the previously reported heterogeneous catalysts, FeO_xPd NPs (Fig. S16, ESI†) and hollow nanocomposite Pd NPs (Fig. S17, ESI†), low yields were obtained (Table 2, entries 14, and 15) for the oxidation of cycloheptanol.[18a, 21a] As a control, we also found the Pd NPs supported by a rigid polypyrrole nanocomposite yielded the corresponding product in low conversion (30%) after 12 h. In case of this catalyst, the Pd NP catalysts cannot be reactive because they are thoroughly coated and immersed in the polymer matrix. The polymer composite support is impermeable to reagents and precludes the diffusion of substrate/products.[18]

Therefore, we concluded the polymer shell in the designed Pd nanocatalysts indeed provide a means of uniformly distributing the Pd NPs throughout the redox reaction between monomer and palladium precursor to ensure the controlled formation of uniform NPs encrusted in the polymer shell.

Table 2. Oxidation of cycloheptanol catalyzed by different supported Pd NPs catalysts.[a]



Entry	Catalyst	Yield (%)[b]
1	Pd nanocatalysts	99
2	Pd nanocatalysts without H_2O_2	15
3	Pd NPs supported on silica layer of core-shell	32
4	No catalysts with H_2O_2	25
5	*N*-(3-Trimethoxysilylpropyl)-PPy supported Pd NPs	30
6	K_2PdCl_4	21
7	Pd NPs prepared by P85	27
8	Pd NPs prepared by F127	29
9	Commercial Pd NPs/C	53
10	Commercial Pd NPs/Charcoal	48
11	Carbon supported Pd NPs	49
12	Mesoporous carbon supported Pd NPs	47
13	SBA15 supported Pd NPs	39
14	Hydroxyapatite supported Pd NPs	67
15	FeO_xPd NPs	35
16	Hollow Pd nanocomposite	43

[a] Reaction conditions: heptanol (0.25 mmol), H_2O_2 30% (0.75 mmol), catalyst (1 mol %), H_2O (2.5 ml), 80 °C, 12 h. [b] The yields were determined by GC-MS with respect to an internal standard (decane).

The presence of the polymer layer on the designed core-shell nanocatalysts is effective for preventing the agglomeration of Pd NPs resulting in the high durability and recycling characteristics of the Pd nanocatalysts. The well-defined polymer matrix accommodates abundant small-sized accessible Pd NPs and serves as a shield to stabilize catalyst NPs for maintaining their activity under oxidative reaction conditions. Reusability of the catalysts is an important criterion for practical applications. To verify this, we investigated magnetic separation and recycling of the designed Pd nanocatalysts (Scheme 2), which was successfully recycled and reused for five consecutive cycles of the oxidation of cycloheptanol (Table 3).

Scheme 2. Magnetic separation and recycling of the designed Pd nanocatalysts.

Upon completion of the reaction the catalyst was easily separated using a magnet, washed with acetone and water and reused in the next reaction. TEM image of the recycled Pd nanocatalysts showed that the nanocatalysts were stable after the recycling (Fig. S18, ESI†). The solution of the fifth reaction runs were analyzed by ICP-AES after workup. The ICP-AES analysis showed that 0.8% of Pd species remained in the reaction solutions. Consequently, the small decrease of catalytic activity seems to result from either incomplete magnetic separation of the Pd nanocatalyst or leaching of Pd species during the consecutive recycling. To investigate the possibility of a continuous oxidation process we screened constant addition of starting materials for five runs without separating the nanocatalysts. The aliquots were drawn from the reaction mixtures every 12 h and analyzed by a GC-MS. The oxidation of cyclooctanol was accomplished with very good yield (Table S2, ESI†). The magnetically recyclable core-shell Pd nanocatalysts can be readily synthesized on a large scale using a simple process. When larger amounts of starting materials (×20) were used, 22.5 g of the Pd nanocatalysts could be obtained from one batch in a standard academic laboratory (Fig. S14, ESI†).

Table 3. Magnetic separation and recycling of the Pd nanocatalysts in heterogeneous oxidation of heptanol.[a]

Cycle	1st	2nd	3rd	4th	5th
Yield of product (%)[b]	99	99	98	95	90

[a] Reaction conditions: heptanol (0.25 mmol), Pd nanocatalyst (1 mol%), 12 h, 80 °C, H_2O_2 30% (0.75 mmol), H_2O (2.5 ml). [b] Yields were determined by GC-MS with respect to an internal standard (decane).

We finally investigate the potential applications and reactivity of the nanocatalysts in other catalytic reactions requiring Pd NPs. Suzuki cross-coupling reaction and reduction of nitroarenes are important chemical reactions in the laboratory and the chemical industries.[19, 20] The designed nanocatalysts showed excellent activity in heterogeneous Suzuki cross-coupling reaction of aryl halides (Table S2, ESI†) and heterogeneous reduction of nitro compounds (Table S3, ESI†). The Suzuki cross-coupling reaction of aryliodides and bromides with phenylboronic acid gave almost quantitative yields in 2 and 4 h, respectively. The attractive features exhibited by the designed magnetically recyclable nanocatalysts enabled to have high catalytic activity for Suzuki reactions in milder reaction conditions and shorter reaction time compared to those required by our previously reported heterogeneous catalysts.[14, 21] In the reduction process for nitro aromatics, the halogen functional groups remained intact under the reaction conditions. The nitro group of nitroarenes with different functional groups using the magnetically recyclable nanocatalysts was selectively reduced to the amine moiety.

Conclusions

In conclusion, we have described novel magnetically retrievable core-shell Pd nanocatalysts for the efficient oxidation of alcohols under base-free reaction conditions in water. The polymer shell of the designed nanocatalysts stabilizes uniform Pd NPs providing high catalytic activity under destructive reaction conditions. This framework accommodates palladium NPs to be condensed on the rings to prevent agglomeration and maintain the catalytic reactivity under oxidative reaction conditions. The magnetic core can be readily utilized for the easy recovery and recycling of the Pd nanocatalysts while it is isolated and protected by impermeable silica shell minimizing any side reactions during catalytic processes. The designed nanocatalysts can be readily synthesized in a large scale and were able to be reused for five consecutive cycles of the oxidation of cycloheptanol. This novel approach will find potential applications in other types of nanocatalyzed reactions involving Pd NPs.

Acknowledgements

We acknowledge financial support by the Research Center Program of Institute for Basic Science (IBS) in Korea.

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Magnetically Recyclable Core-Shell Nanocatalysts for Efficient Heterogeneous Oxidation of Alcohols