

包钯纳米颗粒的中空介孔硅铝酸盐纳米球的合成及其在多步催化反应和尺寸选择催化氢化中的应用

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摘要 最近,具有中空核壳结构的纳米材料在催化领域有着深入的研究和广泛的应用.在本文中,我们使用一种简单易行的方法合成了一种包裹钯纳米颗粒的中空介孔硅铝酸盐纳米球(简称为 Pd@HMAN).首先,通过一种先原位合成钯纳米粒子再对其进行二氧化硅包裹的方法,在 Brij56-环己烷-水的反相胶束中合成了具有核壳结构的包裹钯纳米颗粒的二氧化硅纳米球(简称为 Pd@SiO₂).然后,使用 CTAB, Na₂CO₃ 和 NaAlO₂ 试剂,通过简单的碱性条件下刻蚀 Pd@SiO₂ 的过程,我们成功得到了具有多孔性能的中空核壳型 Pd@HMAN 纳米催化剂.由于硅铝酸盐外壳具有酸催化作用,并且内核钯纳米颗粒又是一种高活性的催化媒介,因此,这种复合的多功能纳米催化剂能够很好的应用于多步催化反应中.此外,通过一个简单的热处理的方法,能够缩小硅铝酸盐外壳上的孔道,我们发现这种孔道调节后的 Pd@HMAN 纳米催化剂在尺寸选择性氢化反应中有很好的应用前景.

关键词 反相胶束;核壳结构;中空核壳结构;钯;多功能纳米催化剂;尺寸选择性催化;催化氢化

Pd Nanoparticles Encapsulated in Hollow Mesoporous Aluminosilica Nanospheres as an Efficient Catalyst for Multistep Reactions and Size-Selective Hydrogenation

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Abstract In this work, yolk-shell structured Pd@hollow mesoporous aluminosilica nanospheres (designated as Pd@HMAN) have been successfully fabricated by a straightforward synthetic route. Core-shell Pd@SiO₂ nanospheres were firstly obtained by silica coating of *in-situ* synthesized Pd nanoparticles in a Brij56-cyclohexane-water reverse micelle system. Simply by alkaline etching of as-prepared Pd@SiO₂ core-shell nanospheres in the presence of CTAB, Na₂CO₃ and NaAlO₂, Pd@HMAN particles with high porosity were obtained. As the mesoporous aluminosilica shells can serve as acid catalysts, and the Pd yolks can be applied to catalytic hydrogenation, the as-prepared Pd@HMAN can be used as a stable multifunctional catalyst for multistep reactions. Moreover, due to their adjustable pore parameters, Pd@HMAN after simple thermal treatment can be further applied in the size-selective hydrogenation.

Keywords reverse micelle; core-shell structure; yolk-shell structure; palladium; multifunctional nanocatalyst; size-selective catalysis; hydrogenation

1 Introduction

During the past decade, yolk-shell structured nanomaterials with functional nanoparticles inside hollow shells have attracted increasing attention in various fields, such as catalysis,^[1] delivery,^[2] and lithium-ion batteries^[3] because of their tailorability and functionality in both cores and hollow shells. As a special type of yolk-shell nanomaterials, hollow permeable shells containing noble metal nanoparticles have emerged as an ideal nanoreactor system

and have been intensively pursued in confined catalysis.^[1a,1b] In yolk-shell structured nanocatalysts containing noble metal nanoparticles, each noble metal nanoparticle isolated by the permeable shell has a relatively homogeneous surrounding environment for the catalytic reaction. The permeable shells can effectively prevent the aggregation and sintering of the encapsulated noble metal cores, and simultaneously allow the fast diffusion of reactants and products. Consequently, this kind of yolk-shell structured nanocatalysts can exhibit excellent catalytic ac-

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tivity and long-term stability.^[4]

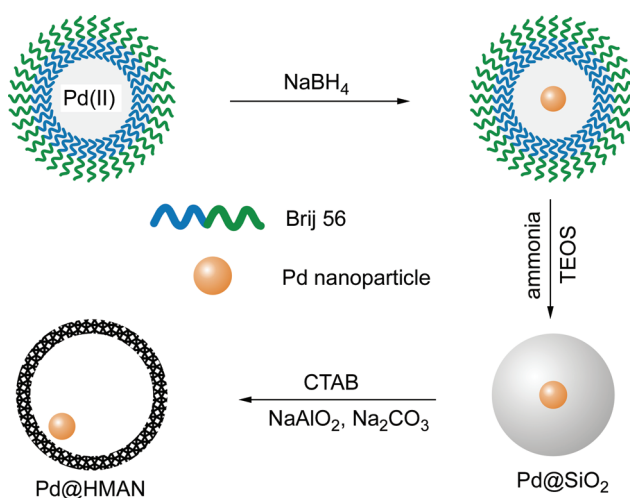
In previous studies, several synthetic strategies, such as hard-templating methods,^[4,5] soft-templating methods,^[6] and selective etching,^[7] have been developed for the synthesis of yolk-shell nanocatalysts containing noble metal nanoparticles. However, most studies focus on synthesis of desired noble metal cores, and rare work succeeds in designing and utilizing catalytically active permeable shells. Since the noble metal yolk is the sole catalytic component, these yolk-shell structured nanocatalysts reported previously were usually applied in single-step reactions.^[1a,1b] If a multifunctional yolk-shell structured nanocatalysts could be applied in the multistep reactions to give desired products in high yields, the number of purification and separation steps and the amount of wastes and solvents can be reduced, and the cost of final products can be reduced consequently.^[8] Furthermore, from the viewpoint of fundamental research and practical application, extending the size-selective catalysis to yolk-shell structured nanocatalysts by tailoring the pore structure of permeable shells is highly desired.^[9] However, until now, size-selective catalysis based on the yolk-shell structured nanocatalysts has received only limited success due to the lack of the effective synthetic methodologies.^[9] It still remains a great challenge to develop an effective synthetic route to multifunctional yolk-shell structured nanocatalysts for multistep reaction sequences and size-selective catalysis.

Herein, we report a selective etching route to fabricate Pd nanoparticles encapsulated in hollow mesoporous aluminosilica nanospheres (*i.e.*, Pd@HMAN). Core-shell structured Pd@SiO₂ nanospheres were firstly obtained by the silica coating of *in-situ* synthesized Pd nanoparticles in a Brij56-cyclohexane-water reverse micelle system. After alkaline etching of Pd@SiO₂ core-shell nanospheres in the presence of cationic surfactant cetyltrimethylammonium bromide (CTAB), Na₂CO₃ and NaAlO₂, Pd@SiO₂ core-shell nanospheres were transformed into Pd@HMAN with uniform pore size distribution. With accessible acidity of permeable aluminosilica shells and catalytically active yolks, the as-prepared Pd@HMAN exhibits a good catalytic performance in the model multistep reaction. More importantly, the shrinkage of mesopores in the aluminosilica shells caused by a simple heat treatment makes Pd@HMAN as a promising nanocatalyst for size-selective hydrogenation.

2 Results and discussion

2.1 Synthesis and characterization of Pd@HMAN catalyst

As illustrated in Scheme 1, the proposed procedures for the synthesis of Pd@HMAN mainly include three steps. In the first step, Pd nanoparticles were *in-situ* synthesized in a reverse micelle system. The reverse micelle system was composed of nonionic surfactant Brij56 (C₁₆H₃₁(OCH₂-CH₂)₁₀OH), cyclohexane, and aqueous solution of H₂PdCl₄. After the dynamic balance of the Brij56-cyclohexane-water reverse micelle system, NaBH₄ was introduced as a reductant to reduce the precursor H₂PdCl₄ to Pd nanoparticles. The confined synthesis of Pd nanoparticles inside the proposed reverse micelle system was demonstrated by the



Scheme 1 Synthetic procedures of Pd@HMAN catalyst

dynamic light scattering measurements (Figure S1). In the second step, NH₄OH solution and silica precursors TEOS was added dropwise into the previous reverse micelle system in turn. After hydrolysis and condensation of TEOS, the Pd@SiO₂ core-shell nanospheres were obtained. In the final step, the as-prepared Pd@SiO₂ core-shell nanospheres were directly converted into the yolk-shell structured Pd@HMAN/CTAB through a simple hot alkaline etching process in the presence of CTAB, Na₂CO₃ and NaAlO₂. After a hydrothermal treatment and CTAB removal process, the final yolk-shell structured Pd@HMAN nanospheres were prepared. In our previous investigation,^[8b] we fabricated a multifunctional Pd/Au@HMAS catalyst which exhibited high catalytic activity and recyclability for the multistep reaction sequences. However, compared with the synthetic strategy designed in this work, our previous design was not straightforward, and the synthetic procedures were thus troublesome.

The morphologies of the as-prepared Pd@SiO₂ core-shell nanospheres and Pd@HMAN nanospheres were characterized by transmission electron microscopy (TEM). As shown in Figure 1a, each of Pd@SiO₂ core-shell nanosphere contains only one Pd nanoparticle at its center. Moreover, these Pd@SiO₂ nanospheres particles have uniform size and shape, most of which are 25 nm in size. After treated with the proposed selective etching process, Pd@SiO₂ core-shell nanospheres were successfully transformed into Pd@HMAN. As revealed by Figure 1b, the as-prepared Pd@HMAN particles possess well-defined yolk-shell structures with movable Pd yolks nicely encapsulated in hollow mesoporous shells. It is well-documented that such one-in-one encapsulation of noble metal nanoparticles in hollow shells can effectively prevent the aggregation of catalytic nanoparticles and therefore significantly improve their catalytic stability.^[1c,4,10] By estimating from TEM image, Pd yolks in the Pd@HMAN have a narrow size distribution around 4.5 nm (Figure 1c). Moreover, the size of Pd yolks was further characterized by X-ray powder diffraction (XRD). As shown in Figure 1d, the XRD pattern of Pd@HMAN can be indexed to face-centered cubic Pd (JCPDS No. 05-0681). The average size of Pd yolks deduced from Scherrer's formula for the strongest peak (111) is about 5.6 nm. The energy-dispersive X-ray spec-

troscopy (EDX) spectrum (Figure S2) reveals that the hollow shells of Pd@HMAN contains Si, Al, O, and Na elements, which agrees well with our previous report on the synthesis of hollow mesoporous aluminosilica spheres by the same alkaline etching process.^[8b]

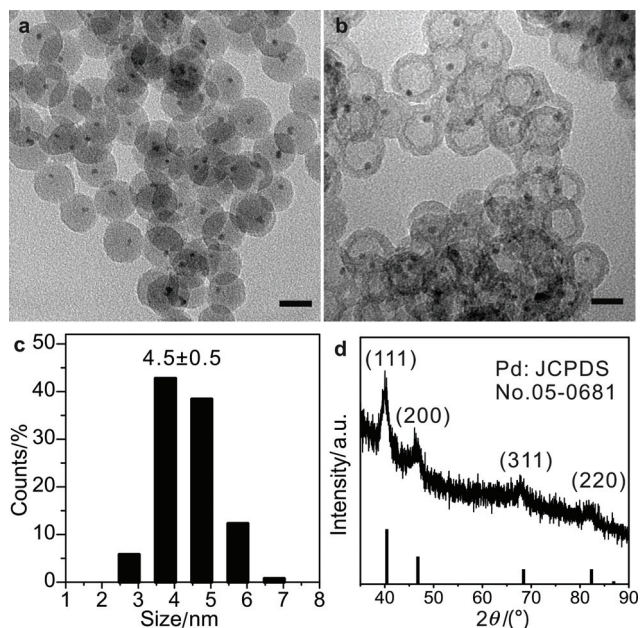


Figure 1 TEM images of Pd@SiO₂ (a) and Pd@HMAN (b), scale bars are 20 nm; (c) size distribution of Pd yolks of Pd@HMAN; (d) XRD pattern of Pd@HMAN.

To be an accessible nanoreactor for confined catalysis, a permeable shell is essential for yolk-shell nanocatalysts containing noble metal nanoparticles. The porosity of Pd@HMAN was investigated by N₂ adsorption-desorption measurements. As shown in Figure 2a, Pd@HMAN exhibit a type IV isotherm with a type H2 hysteresis loop, characteristic of mesoporous materials. The Brunauer-Emmett-Teller (BET) surface area and pore volume of Pd@HMAN are 326.9 m²/g and 0.93 cm³/g, respectively. The pore distribution of Pd@HMAN was obtained from the analysis of the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method. As shown in Figure 2b and Figure S3, Pd@HMAN had a bimodal pore size distribution at 2.4 and 23 nm. The dominating pore at 2.4 nm (Figure 2b) is attributed to the mesoporous pores in the shell walls. Such a pore size distribution reveals that the formation mechanism of Pd@HMAN is similar to our previous report on hollow mesoporous aluminosilica spheres synthesized using CTAB to direct the formation of mesopores.^[8b] Larger pores around 23 nm (Figure S3) is likely caused by the interior cavities created by etching of silica. The high surface area and porosity make the as-prepared Pd@HMAN as a promising candidate for catalytic applications.

2.2 Pd@HMAN for multistep reactions

Benzimidazole derivatives are important functional compounds due to its attractive antiviral, antiulcer, and anticancer properties.^[11] However, previously reported methods for the synthesis of benzimidazole derivatives still have some disadvantages, such as high cost, long reaction

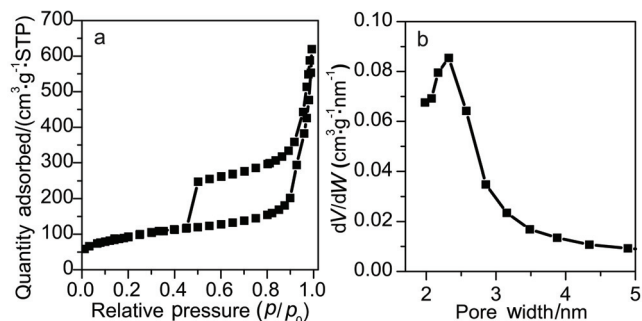


Figure 2 Nitrogen adsorption-desorption isotherm (a) and pore size distribution (b) of Pd@HMAN.

time, harsh reaction conditions, and inconvenience in separation of the products from the reaction mixtures.^[11] As the mesoporous aluminosilica shells can serve as acid catalysts, and the Pd yolks can be applied to catalytic hydrogenation, the as-prepared Pd@HMAN material is a promising multiple catalyst.

To demonstrate that the yolk-shell structures obtained in this work can be used as catalysts for multistep reactions, we chose a synthetic route involving an acid catalysis and subsequent catalytic hydrogenation for the synthesis of a key intermediate of benzimidazole derivatives 2-(4-aminophenyl)-1*H*-benzimidazole (Figure 3a). The intermediate and the final product were identified by mass spectrometry and ¹H NMR. As illustrated in Figure 3b, after the two-step

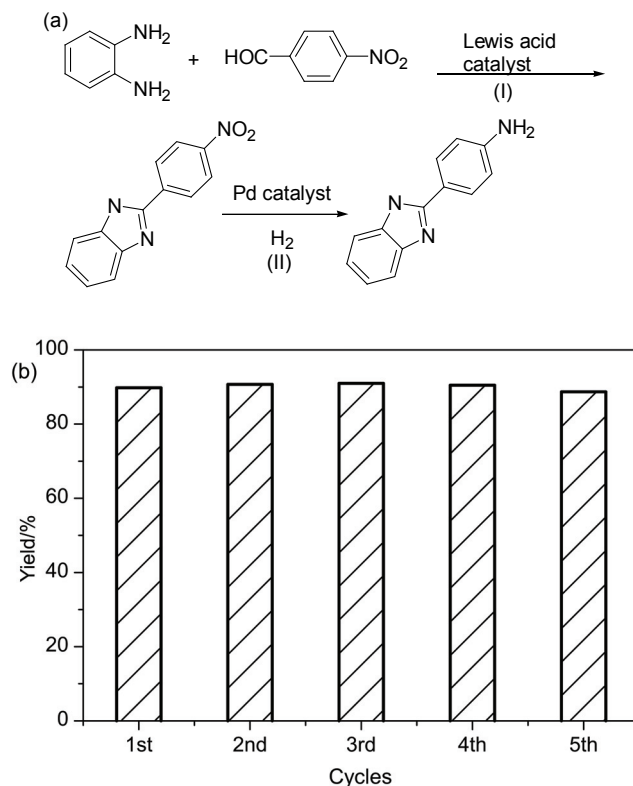


Figure 3 (a) Schematic illustration of multistep reaction sequences involving an acid catalysis and subsequent catalytic hydrogenation for synthesis of 2-(4-aminophenyl)-1*H*-benzimidazole, (b) Synthesis yields of 2-(4-aminophenyl)-1*H*-benzimidazole in the 5 successive reactions using Pd@HMAN catalyst.

reaction sequences had been run using Pd@HMAN as the catalyst, the reactant 4-nitrobenzaldehyde was consumed completely and 90% of the final mixture was the desired product 2-(4-aminophenyl)-1*H*-benzimidazole. In the previous reports on the two-step synthesis of 2-(4-aminophenyl)-1*H*-benzimidazole using non-recyclable catalysts, the synthetic procedure was somewhat time-consuming and the total yield was only about 80%.^[11b] More importantly, the Pd@HMAN catalyst exhibited a good recyclability. The catalyst after catalytic reaction was separated by centrifugation, rinsed with methanol, and redispersed into methanol for the catalytic cycle. The yield of 2-(4-aminophenyl)-1*H*-benzimidazole in the 5th cycle was found still about 90%, confirming that the unique yolk-shell structure endowed the Pd@HMAN catalyst with excellent stability and recyclability.

2.3 Thermally treated Pd@HMAN for size-selective hydrogenation

Size or shape-selective catalysis is an important and basic concept in the field of catalysis. Recently, controlling the pore sizes in the shell walls of some core-shell or yolk-shell structured catalysts to realize size-selective reaction has attracted much attention.^[11b,9] As the 2.4 nm of mesopores is capacious for many small molecules, we firstly shrunk the mesopores in shell walls of Pd@HMAN by a facile heat treatment. After treating at 700 °C for 2 h in air, no obvious change in the structure of the thermally treated Pd@HMAN was observed (Figure S4). The average size of Pd yolks in the thermally treated Pd@HMAN catalyst was calculated to be about 6.0 nm based on its XRD pattern (Figure S5), agreeing well with the crystallites size of Pd nanoparticles in the untreated Pd@HMAN catalyst. As shown in Figure 4a, similar to the untreated Pd@HMAN, the BET surface area and pore volume of the thermally treated Pd@HMAN are 382.5 m²/g and 0.87 cm³/g, respectively. Interestingly, the pore distribution curve calculated by the Horvath-Kawazoe method (Figure 4b) reveals that the thermally treated Pd@HMAN has a narrow micropore size distribution around 1.1 nm, indicating that the mesopores in shell of Pd@HMAN have successfully been shrunk after the thermal treatment.

In order to evaluate the possibility to apply the thermally treated Pd@HMAN catalyst for size-selective catalysis, styrene and *trans*-1,2-diphenylethylene, were chosen as the model reactants for size-selective catalytic hydrogenation. As shown in Figure 4c, the thermally treated Pd@HMAN catalyst exhibited high activity with a conversion of styrene over 99.9% after 0.5 h, with no significant difference from the untreated Pd@HMAN catalyst. However, regarding the hydrogenation reactions of *trans*-1,2-diphenylethylene (Figure 4d), the thermally treated Pd@HMAN catalyst had a much lower activity than the untreated catalyst. It is notable that the untreated Pd@HMAN catalyst had a high activity with a conversion of 98% for *trans*-1,2-diphenylethylene after 5 h. Using the thermally treated Pd@HMAN catalyst under the same reaction conditions, a rather low conversion of 13% was achieved. These results show that the pore channels of Pd@HMAN catalyst shrunk a lot after the thermal treatment and were thus only accessible by relatively small-size molecules. Consequently, we believe that the thermally treated Pd@HMAN has potential

applications in the size-selective catalytic reactions.

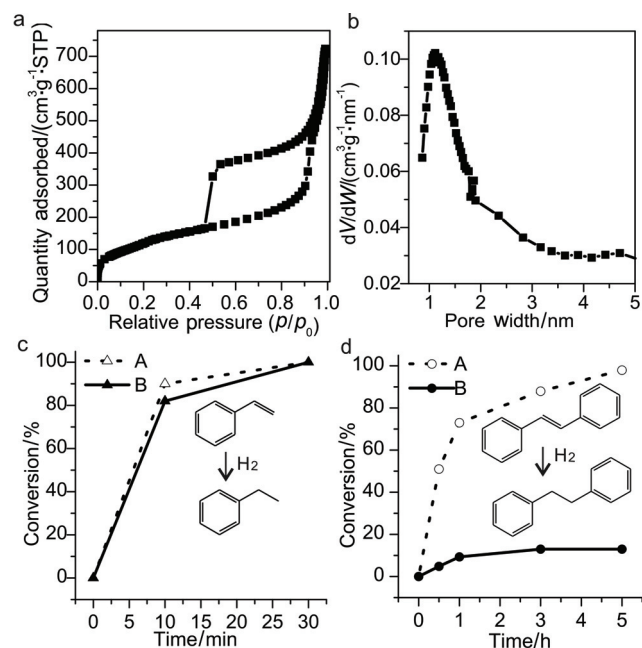


Figure 4 Nitrogen adsorption-desorption isotherm (a) and pore size distribution (b) of thermally treated Pd@HMAN, catalytic hydrogenation of the styrene (c) and *trans*-1,2-diphenylethylene (d) using different catalysts (A: Pd@HMAN, B: heat-treated Pd@HMAN).

3 Conclusion

In summary, we have developed a facile route to prepare yolk-shell structured Pd@HMAN. In the proposed Brij56-cyclohexane-water reverse micelle system, we obtained uniform Pd@SiO₂ core-shell nanospheres. By using as-prepared Pd@SiO₂ as templates, yolk-shell structured Pd@HMAN was prepared through an alkaline etching in the presence of cationic surfactant CTAB and aluminate species. With the unique yolk-shell structure and composition, the as-prepared Pd@HMAN is an ideal candidate for nanoreactor. The as-prepared Pd@HMAN has been successfully used as a multifunctional catalyst, which exhibit high catalytic performances and recyclability in two-step reaction sequences for the synthesis of benzimidazole derivatives. As the pore parameters of Pd@HMAN can be adjusted by a facile heat treatment, the heat-treated Pd@HMAN has been further applied in the size-selective hydrogenation. We believe that the synthesis and potential applications of Pd@HMAN reported in this contribution would open new opportunities for yolk-shell structured nanomaterials.

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