Hollow silica spheres encapsulating Pd nanoparticles and aminopolymers as nanoreactors for semihydrogenation of alkynes

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Abstract: The semihydrogenation reaction of alkynes to produce alkenes is one of the most important and fundamental reactions for the synthesis of bulk and fine chemicals. Here we report the synthesis of hollow silica spheres encapsulating Pd nanoparticles and aminopolymers which act as selective and reusable heterogeneous catalyst in the semihydrogenation of alkynes. The synthesis was performed by a self-assembly approach using linear- or branched-type poly(ethyleneimine) as a self-template. The synthesized organic-inorganic hybrid showed excellent alkene selectivity in the semihydrogenation of internal and terminal alkynes owing to the ability of the silica shell to prevent the leaching of the encapsulated components.

Keywords: Yolk-shell nanostructure, Aminopolymer, Pd nanoparticles, Semihydrogenation.

1. Introduction

Hollow silica spheres encapsulating catalytic components in their internal void spaces (so-called “yolk–shell” nanostructures) are emerging class of nanostructured materials. The enclosed void space is expected to be useful for encapsulation and compartmentation of guest molecules, and the outer silica shell acts as a physical barrier to protect them from the surrounding environment or endow them with a molecular sieving property. Furthermore, the tunability and functionality in the void and the shell regions can offer new physicochemical/catalytic properties, rendering them attractive nano-platforms for catalyst design[1-3].

The semihydrogenation reaction, which converts alkynes to alkenes, is one of the most important and fundamental reactions for the synthesis of bulk and fine chemicals. Lindlar catalyst (Pd/$CaCO_3$ treated by Pb salts) has been a prototype heterogeneous catalyst; however, it has some serious drawbacks such as high toxicity of Pb species and the low alkene selectivity toward terminal alkynes. Alternatively, Pd supported on poly(ethyleneimine) (Pd/PEI) and those supported on silica have recently been studied[4], however, they still suffer from leaching of Pd NPs and aminopolymers during catalytic cycles, resulting in a low selectivity for alkenes and reduced reusability of catalyst.

In this study, we report the synthesis of hollow silica spheres encapsulating Pd nanoparticles (NPs) together with aminopolymers inside the hollow cavities (Pd+PEI@HSS) and application in the semihydrogenation of alkynes with H_2 to produce alkenes. The synthesized hybrid aminopolymer-silica materials could act as efficient and reusable heterogeneous catalyst in the semihydrogenation of internal and terminal alkynes.

2. Experimental

Pd+PEI@HSS was synthesized by a self-assembly approach using linear- or branched-type poly(ethyleneimine) as a self-template. $NaBH_4$ as a reducing agent was added into the ethanolic solution containing Pd precursor and PEI to obtain brownish solution. To this solution was added tetraethylorthosilicate (TEOS) as a Si source, followed by aging at ambient conditions to yield Pd+PEI@HSS. Synthesis was performed by using PEI with different molecular weights (M_w = 600 ~ 10,000) and by adding different amounts of TEOS to investigate the effects of synthetic conditions on the morphology and the catalytic performance of the final solids.

3. Results and discussion

The FE-SEM and TEM images show that Pd+PEI@HSS synthesized using linear-type PEI is composed of dispersed hollow spheres with an average particle size of ca. 160 nm containing Pd NPs in their void spaces (Figure 1). The silica shell thickness was determined to be ca. 50 nm, and the average diameter of Pd NPs was determined to be ca. 9 nm. Smaller silica particles with thinner silica shell were obtained when branched-type PEI was used as an organic template. Elemental mapping images clearly verified that the Pd+PEI@HSS contains aminopolymers in the void space. N_2 adsorption measurements confirmed the existence of randomly-arranged micro-pores (ca. 1 nm in diameter) in the silica shell region.

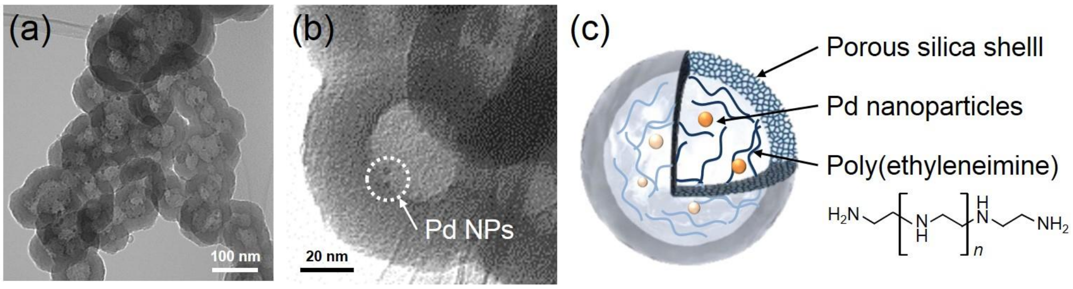

Figure 1. (a,b) TEM images and (c) schematic illustration of Pd+PEI@HSS (synthesized with linear PEI).

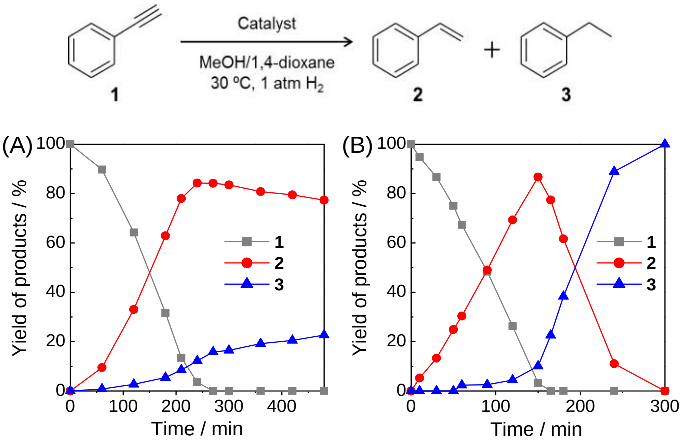

Figure 2. Reaction kinetics in the semihydrogenation of phenylacetylene using (A) Pd+PEI@HSS (linear PEI) and (B) Pd+PEI@HSS (branched PEI). *Reaction conditions:* catalyst (Pd: 0.5 mol%), phenylacetylene (1.0 mmol), MeOH (5 mL) + 1,4-dioxane (5 mL), H_2 (1 atm), 30 °C.

Pd+PEI@HSS exhibited an excellent selectivity in the semihydrogenation of diphenylacetylene, affording the corresponding alkene with more than 95% alkene selectivity (*cis*/*trans* = 95:5), which was far superior to that of Pd@HSS (without PEI) and even higher than those of the conventional Lindlar catalyst and Pd/PEI, demonstrating that the encapsulation of PEI drastically improves the alkene selectivity. The hybrid catalyst was applicable to terminal alkynes, phenylacetylene, as well; styrene was produced with 84% selectivity when Pd+PEI@HSS synthesized with linear PEI was used, whereas Pd+PEI@HSS synthesized with branched PEI afforded a lower alkene selectivity (Figure 2). The Pd+PEI@HSS having an optimum shell thickness was reusable over at least 5 catalytic cycles without any significant loss of activity and selectivity.

4. Conclusions

A new type of hybrid aminopolymer-silica composite with yolk–shell nanostructure was synthesized via a facile synthetic approach. Such a yolk-shell nanostructure could act as efficient and reusable heterogeneous catalyst in the semihydrogenation of alkynes, giving a markedly improved alkene selectivity compared with the conventional Pd-based catalysts. The improved catalytic performance was due to the ability of the silica shell to strongly stabilize Pd NPs and aminopolymer[5].

References

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