

Tailored design of Pd catalyst supported on chemically modified silica hollow microspheres for NBR hydrogenation

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Abstract: silica hollow microspheres (SHMs) with penetrating macropores in the shells are prepared by a simple one-step method with water/oil/water ternary phase emulsion system, then the surface of SHMs was modified with N-Propylethylenediamine (N-SHMs) and the Pd components were bound to the surface by means of the coordination of -NH₂- and -NH- ligands (Pd/N-SHMs). The result showed that the catalyst possessed well-dispersed small Pd nanoparticles with the average size of 2 nm and showed higher activity of 95.0% for hydrogenation of NBR under mild condition (60 °C, 2.0 MPa H₂, 1 h).

Keywords: macropores, modified, small Pd nanoparticles.

1. Introduction

The hydrogenation of nitrile-butadiene rubber (NBR) to HNBR is important to improve its properties and performance and extend its wide application, which can be realized by heterogeneous or homogeneous processes depending on the nature of the catalyst.^[1] Homogeneous hydrogenation has high activity but the removal of expensive catalysts is difficult; and the residual catalysts in the product can cause polymer degradation. Heterogeneous catalytic system can overcome the shortage and easily achieve catalysts recycling, but its hydrogenation rate and degree are not satisfied, especially for high molecular weight NBR.^[2] The ideal heterogeneous catalysts for NBR hydrogenation require the macroporous structure to enhance the molecular diffusion as well as the well-dispersed active sites to improve the activity.^[3] Herein, we have carefully designed silica hollow microspheres (SHMs) with penetrating macroporous shells as the support to prepare Pd-based supported catalyst via the chemical modification method to control the particle size and dispersion, as shown in Fig. 1. Our work will help us to understand the heterogeneous hydrogenation of macromolecular polymers, which will lay a foundation for the further industrial application.

2. Experimental

A typical reaction procedure for the synthesis of SHMs in a W/O/W emulsion system has been reported previously.^[4] Then the synthesized SHMs was modified with N-[3-(Trimethoxysilyl)propyl]ethylenediamine (EDAS) and the palladium components were bound to the SHMs surface subsequently. The hydrogenation reaction was carried out in an agitated autoclave reactor with 1.0 g NBR dissolved in 100 mL acetone. The reaction temperature and H₂ pressure were maintained at 60 °C and 2.0 MPa, respectively, and the agitation rate was kept at 800 rpm. After reaction for 2 h, the hydrogenated NBR solution was centrifuged to separate the catalyst from the system.

3. Results and discussion

The morphology and structure of the particles were characterized by SEM. It is intriguing to find that the microsphere is hollow and the shells are multilayered architectures with an abundance of ultra-large macropores as shown in Fig. 2A. Fig. 2B displays FTIR spectrum for SHMs and N-SHMs to identify EDAS groups attached to the silica framework. The absorbance at 965 cm⁻¹ for pristine SHMs assignable to the terminal silanol (Si-OH) groups decreases after the surface modification, implying the successful replacement of Si-OH with EDAS. Moreover, new peaks at 2935, 1474 and 1589 cm⁻¹, corresponding to the

asymmetric and scissoring vibration of the C-H groups of silylating agents and N-H scissoring vibration are present in N-SHMs, further verifying the successful grafting of EDAS to the surface of SHMs. Pd/N-SHMs (Fig. 2C) displays evenly distributed Pd nanoparticles with quite uniform particle size and no aggregation of Pd over N-modified support. The particle size distribution obtained by counting more than 200 particles from TEM images presents a quite narrow particle size distribution centered at 1.85 nm. NBR with a large molecular weight of 360,000 was used to evaluate the catalytic performance, and the results show that the high hydrogenation of degree with 100% selectivity to C=C can be obtained at mild conditions (60 °C, 2.0 MPa H₂) only within 60 min.

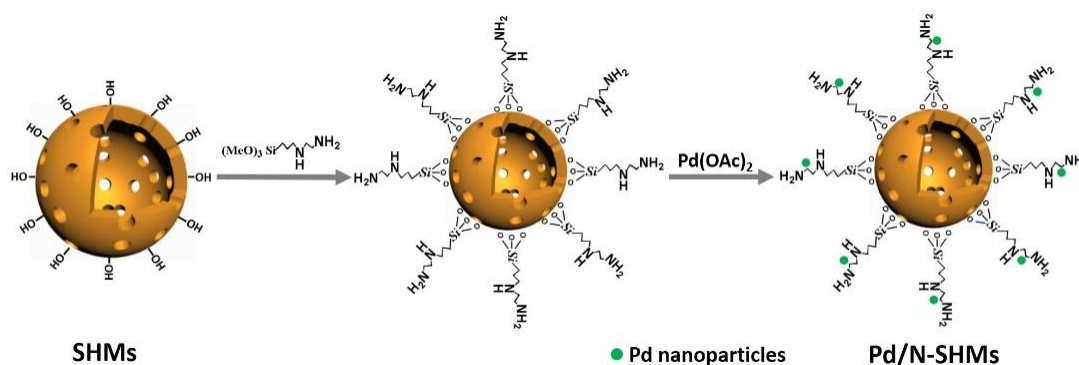


Figure 1. Preparation procedure of Pd/N-SHMs.

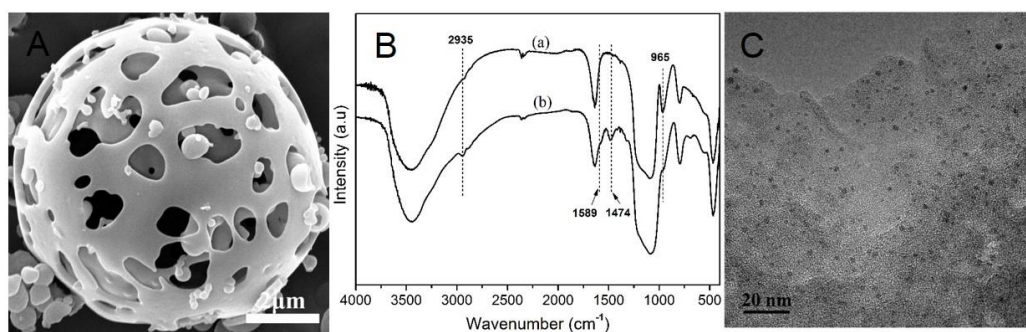


Figure 2. SEM image of SHMs (A), FTIR spectra of SHMs and N-SHMs (B) and TEM images of Pd/N-SHMs (C).

4. Conclusions

Owing to the enhanced support-metal interaction, Pd/N-SHMs catalyst based on N-modified silica with penetrating macroporous shells has smaller Pd particle sizes, higher metal dispersion. And our newly proposed SHMs support is effective for the macromolecular reaction due to the macropores in the shell, which can minimize the resistance of pore diffusion and are favorable for the quick diffusion of NBR molecules.

References

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