



Macroporous hollow silica microspheres-supported palladium catalyst for selective hydrogenation of nitrile butadiene rubber



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ABSTRACT

A potential high durable heterogeneous catalyst for the industrial selective hydrogenation of nitrile butadiene rubber (NBR) has been established by immobilizing palladium (Pd) nanoparticles on macroporous hollow silica (MHS) microspheres in the present work. Compared with the Pd nanoparticles supported on macroporous hollow silica (Pd/MHS) via conversional incipient wetness impregnation with different free chelating reagents (HCl or EDTA) catalysts, the Pd nanoparticles supported on the modified macroporous hollow silica (Pd/M-MHS) catalyst showed better distribution of Pd nanoparticles and catalytic performance. High hydrogenation degree (HD) toward the $-\text{CH}=\text{CH}-$ group of 97% was achieved in acetone solution at 70 °C with H_2 pressure of 4.5 MPa for 6 h, while the nitrile ($-\text{C}\equiv\text{N}$) group had not been hydrogenated in the reaction. And there was no obvious change in the relative molecular weight and polydispersion index of the product in comparison with the raw NBR. The HD for the 5th reuse was 90.5%, remaining more than 93% of its HD for the original time, demonstrating its high durable activity.

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1. Introduction

Recently, hydrogenated nitrile butadiene rubber (H-NBR), which is obtained by the selective hydrogenation of nitrile butadiene rubber (NBR), has attracted great interests in the automobile, oil field, and other industries, due to its excellent oil and chemical resistance, good heat, pressure and ozone resistance, especially at elevated temperature. The selective hydrogenation of the $\text{C}=\text{C}$ double bonds in NBR but not $-\text{C}\equiv\text{N}$ groups mainly enhances its heat, ozone and weathering resistance, simultaneously keeping its oil resistance [1]. Thus, it possesses both oil and fuel resistance properties of NBR and the heat and oxidation resistance of EPDM rubber.

Both homogeneous and heterogeneous catalysts have been used for the selective hydrogenation of NBR. Comparably speaking, the homogeneous catalysts possess higher hydrogenation activity, and the hydrogenation degree >99% could be achieved with less catalyst [2]. However, the catalysts could be partially recovered from the H-NBR latex [3], leading to high-cost, waste, and even the damaged performance of the H-NBR. Thus, the heterogeneous catalysts are expected as more potential ones for the industrial production of H-NBR, owing to the advantage of easy to recycle and reuse.

Up to date, many heterogeneous catalysts have been developed for the selective hydrogenation of NBR, by immobilizing palladium [4,5] or rhodium [6–8] nanoparticles on various supporters, such as clays [4,5], carbon nanotubes (CNTs) [6], SiO_2 [7], graphite oxide sheets [8], etc. It has been reported that mass transfer of hydrogen cannot account for the rate-determining step of hydrogenation of the NBR latex [9]. Although the micro-/mesoporous nanomaterials could provide high surface area as catalyst supports, polymer molecules can hardly enter into their mesopores and be hydrogenated on the active sites subsequently [10], as the polymer size in solution changes from meso- to macro- size region, influenced by molecular weight of polymer, solvent, concentration, and temperature. So it is speculated that the hydrogenation could have occurred only at the active sites in the external surface of the catalyst, but not the ones in the pores. In order to solve the pore size limitation for macromolecule diffusion and reaction, silica microspheres with ultra wide pore size [11] or size-tunable penetrating macroporous shells [12] have been designed for the hydrogenation of polystyrene.

Another important factor is the durability of the heterogeneous catalysts, which affects their reusability. To enhance the binding effect between catalytic active components and supports, the supports have been usually surface-modified to improve their affinity, especially for the metal-based catalysts [13–15]. For the selective heterogeneous hydrogenation of NBR, Yue's group immobilized Rh

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nanoparticles onto CNTs or SiO₂ with polyvinylpyrrolidone (PVP) [6] or 3-aminopropyl-rimethoxysilane (APTS) [7] as a surface modifier, respectively.

In the present work, a high durable heterogeneous catalyst, Pd nanoparticles supported on macroporous hollow silica microspheres (Pd/MHS), was developed for the selective hydrogenation of NBR. The effect of the immobilizing methods on the distribution of Pd nanoparticles in the resultant catalysts and their catalytic performance were investigated in detail. Thus, a potential high durable heterogeneous catalyst for the industrial selective hydrogenation of NBR has been developed.

2. Experimental

2.1. Materials and reagents

Nitrile-butadiene rubber (NBR1806), a pilot product from Lanzhou Petrochemical Research Center, Petrochemical Research Institute, PetroChina Co. Ltd. with acrylonitrile content of 18.41%, M_w of 26.4×10^4 and M_w/M_n of 4.52, and water < 0.5%, was used directly without any pretreatment.

Sodium silicate solution (SiO₂ content of 26 wt.%) was purchased from Beijing Hongxing Chem. Co., Ltd. (Beijing, China). 1-[3-(Trimethoxysilyl)propyl]urea (94.0%) was purchased from J&K Scientific Ltd. Span 80, Tween 80, n-hexane, tetrahydrofuran, dichloromethane, ethanol, acetone, PdCl₂, Pd(OAc)₂, ethylene diamine tetraacetic acid tetrasodium (EDTA-4Na), HCl (36.5 wt.%) and NH₄HCO₃ were analytical grade reagents and used directly without any pretreatment. Double-distilled water was used throughout.

2.2. Macroporous hollow silica (MHS) microspheres

The macroporous hollow silica (MHS) microspheres were prepared as support via a simplified ternary W O/W⁻¹ emulsion system [11], in which the ternary phases were the inner water phase (IWP, 36 mL of sodium silicate solution), oil phase (OP, 36 mL n-hexane containing 0.75 g Tween 80 and 0.75 g Span 80), and outer water phase (OWP, 100 mL of 2 mol/L NH₄HCO₃ aqueous solution), respectively.

Typically, the OP and IWP were emulsified at 10,000 rpm for 1 min. Then the resultant binary emulsion was added into the OWP to form a ternary W O/W⁻¹ emulsion. After the ternary W O/W⁻¹ emulsion was stirred vigorously at room temperature for 2 h, the precipitate was filtered, and washed with water for two times and ethanol for three times, finally dried at 100 °C.

2.3. Pd/MHS catalysts

The Pd nanoparticles supported on macroporous hollow silica microspheres (Pd/MHS) were prepared by the conversional incipient wetness impregnation with different free chelating reagents (HCl or EDTA) or immobilization after surface-modified with chelating groups.

2.3.1. Impregnation with HCl solution

0.438 g (2.47 mmol) PdCl₂ was dissolved in 20 mL of 4 mol/L HCl aqueous solution. Then, the MHS microspheres (5.0 g) were added into the solution to impregnate Pd(II) ions. The resultant solid was dried at room temperature and calcined in air atmosphere at 500 °C for 3 h. Finally, the solid was reduced in a H₂ flow at 120 °C for 2 h [12,16]. The theoretical Pd content in the Pd_{HCl}/MHS was 5.0%.

2.3.2. Impregnation with EDTA solution

The Pd_{EDTA}/MHS catalyst was prepared with the same procedure as for the Pd_{HCl}/MHS presented above, except that EDTA-4Na

(molar ratio to PdCl₂ of 1:1) was added in the solution as chelating reagent.

2.3.3. Chelating on modified MHS microspheres

Firstly, the MHS microspheres were modified with 1-[3-(trimethoxysilyl)propyl]urea to introduce surface chelating groups [17], by dispersing 5.0 g MHS microspheres and 2.6 g (11.7 mmol) 1-[3-(trimethoxysilyl)propyl]urea in 100 mL toluene, and stirring at 80 °C for 3 h. The modified MHS microspheres (M-MHS) were separated by centrifugation, washed with toluene and ethanol in turn, and dried in vacuum at room temperature.

Then the Pd/M-MHS catalyst was fabricated by immobilizing Pd nanoparticles onto the M-MHS microspheres. The M-MHS microspheres (5.0 g) were dispersed into 80 mL toluene. After a 25 mL dichloromethane solution containing 0.554 g (2.47 mmol) Pd(OAc)₂ was added into the dispersion, the mixture was stirred at room temperature for 14 h until the solution became colorless. Finally, the product was separated and reduced as the above procedure. The theoretical Pd content in the Pd_{HCl}/MHS was 5.0%.

For comparison, the Pd/M-MHS catalysts with theoretical Pd content of 3.0% and 8.0% were also prepared via the similar procedure.

2.4. Hydrogenation of NBR

The selective hydrogenation of NBR with the designed catalysts was carried out in a 500 mL agitated autoclave reactor [5]. In a typical experiment, 1.0 g Pd/MHS catalyst and 100 mL acetone solution containing 1.0 g NBR were added into the autoclave reactor. The reactor was sealed and flushed with N₂ to remove air and then with H₂ (99.999%) to remove N₂. The mixture was stirred at 1200 rpm at 70 °C with H₂ pressure of 4.5 MPa for 6 h. Finally, the mixture was centrifuged to separate the catalyst from the solution, and the hydrogenated product was precipitated into ethanol, washed with ethanol for several times, and dried at 105 °C. Hydrogenation degree (HD) was determined with the Bromo-Iodometry method according to GB1676-81 (Chinese National Standards) [18].

Furthermore, the stability and reusability of the Pd/MHS catalysts was evaluated under the same reaction condition, by comparing the catalytic performance of the reused catalyst, which was separated from the product, washed with acetone several times, and dried under vacuum at room temperature.

2.5. Analysis and characterization

The structure of the H-NBR and NBR samples was characterized by ¹H NMR spectroscopy and infrared (IR) spectroscopy. ¹H NMR spectra were recorded on a JNM-LA 300WB FT-NMR spectrometer (JEOL, Tokyo, Japan), with CDCl₃ as solvent. IR spectra analysis was performed on a Magna-IR 560 E.S.P Fourier transform infrared spectrophotometer (FT-IR, Nicolet, USA) in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹, with KBr method.

Phase identification of the catalysts was carried out by qualitative X-ray diffraction (XRD, BRUKER D8 Advance Diffractometer) using Ni-filtered CuKα radiation and operating at 40 kV and 30 mA. The catalysts were scanned in the 5°–80° (2θ) interval at a scanning rate of 0.5°/min.

The morphology and particle size of the MHS microspheres and final Pd/MHS catalysts were characterized with a field emission scanning electron microscope (FE-SEM, FEI Quanta 200F) at an accelerating voltage of 15 kV after sputter coating with gold, and a scanning transmission electron microscope (STEM, FEI Tecnai G2 F20) operated at 200 kV on a carbon-coated copper grid.

The Pd contents in the Pd/MHS catalysts and the H-NBR products were determined with inductively coupled plasma atomic emission spectroscopy (ICP-AES).

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