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Short communication

The mesopore-elimination treatment and silanol-groups recovery for macroporous silica microspheres and its application as an efficient support for polystyrene hydrogenation

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ABSTRACT

Supported Pd catalyst with an enhanced catalytic performance for polystyrene hydrogenation was successfully prepared by using macroporous silica microspheres (MSM) as the support. In order to eliminate the macromolecular diffusion limitation and improve the metal utilization, MSM was treated with steam at 800 °C first to remove mesopores and then refluxed with aqueous solutions to increase Si—OH groups on the surface for Pd immobilization. The optimum support was obtained after the steam treatment for 2 h and using ammonia solution as reflux liquors, and the corresponding catalyst showed superior hydrogenation activity with a high conversion of 95%.

1. Introduction

Polymer hydrogenation is an important process to prepare elastomeric and thermoplastic materials with unique properties and special structures [1–5]. Hydrogenated polymers exhibit highly improved oxidation resistance, thermal stability, solvent resistance, weather resistance, and corrosion resistance, etc., and thus have important practical applications in the field of petroleum, automobiles, machinery, aviation aerospace and other industrial fields [6–8]. Because of the difficulty of catalyst-product separation, the homogeneous catalytic process is usually highly cost and the product quality could also be affected by the residual catalysts. Therefore, heterogeneous catalysts are far more interesting than homogeneous ones from the industrial point of view due to its facile separation and recyclability [9–11]. However, for the macromolecular reaction, the key factors affecting the catalysts performance are the molecular diffusion and the accessibility to the active sites [12,13]. Thus, it is vital and meaningful for the tailored design and controllable synthesis of novel supported macroporous catalysts to achieve an efficient conversion for macromolecules.

The heterogeneous catalysts for macromolecular reactants underwent an era from non-porous to microporous then to meso- or macroporous. Macroporous materials inevitably have abundant micro or mesopores which can provide high specific surface area for the loading of active metals, but cannot allow macromolecules to enter to access the active sites, resulting in a low metal utilization [14–17]. Therefore, how to improve the metal utilization and enhance the active sites accessibility is a big challenge. Herein, macroporous silica microspheres (MSM) with hollow structure have been successfully synthesized through the ternary water/oil/water (W/O/W) emulsion system, and as shown in Scheme 1, the prepared materials are treated with 100% steam at 800 °C for a certain time and then refluxed with aqueous solutions to remove mesopores and recover silanol groups on the surface. The pretreated MSM material is used as a superior support to load Pd nanoparticles (NPs) with the help of ethylene diaminetetraacetic acid (EDTA) to obtain Pd/MSM catalyst which exhibits an enhanced catalytic performance for polystyrene (PS) hydrogenation.

2. Experimental

2.1. Materials

Polystyrene (M_w = 250,000) was purchased from Sigma-Aldrich Company, Ltd. Sodium silicate solution (Na_2SiO_3, 11.3 wt%) and sodium polyacrylate (M_w = 30,000) were purchased from Beijing Hongxing Chemical Company, Ltd. Span 80, Tween 80, n-hexane, cyclohexane, tetrahydrofuran, chloroform, $PdCl_2$, EDTA and NH_4HCO_3

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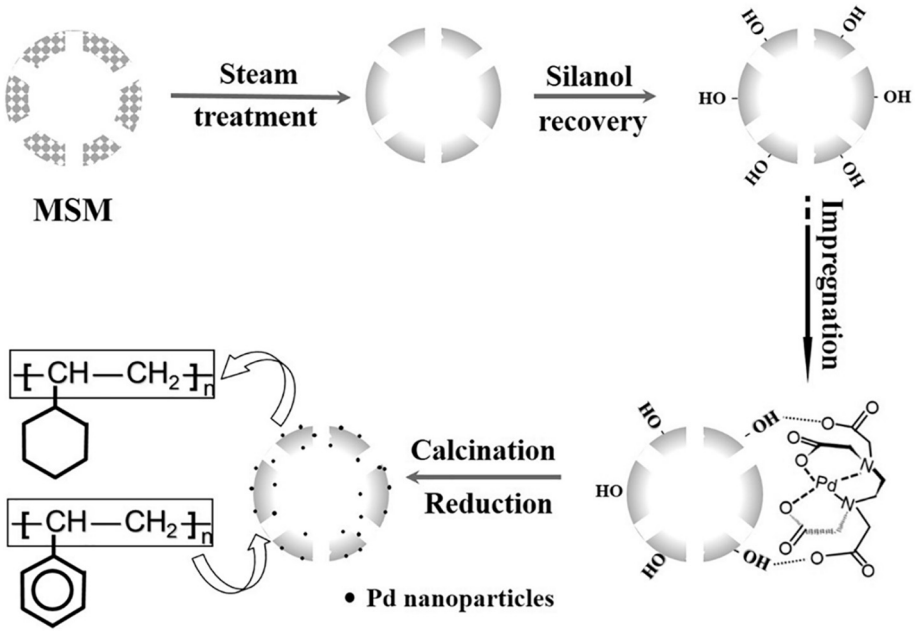

Scheme 1. Preparation procedure of Pd/MSM.

were obtained from Beijing Modern Eastern Fine Chemicals Company, Ltd. All chemicals were used directly without any purification.

2.2. Catalyst preparation

MSM materials were synthesized via a ternary W/O/W emulsion system as described previously [17], the detailed description of which can be found in the Supplementary material. Then, the steam treatment was performed by exposing MSM to pure steam (100% water vapor) at 800 °C for 0, 1, 2, 3 and 4 h, which were denoted as T0-MSM, T1-MSM, T2-MSM, T3-MSM and T4-MSM, respectively. After that, T2-MSM was treated with different aqueous solutions by refluxing at 100 °C for 8 h to increase the surface silanol groups and the resulting samples were washed with deionized water and dried at 120 °C for 5 h. The aqueous solutions used for the refluxing treatment were ammonia water solution, deionized water and nitric acid solution, and the corresponding treated samples were named as Ram-MSM, Rdw-MSM and Rnc-MSM, respectively. Pd/MSM catalysts were prepared as follows: 0.82 g of $PdCl_2$ and 1.31 g of EDTA were added into 30 mL of deionized water and stirred for 5 h to form a homogeneous solution; then, 10 g prepared support was added into the solution for impregnating Pd, the thus-obtained solids were dried and then calcined in air at 773 K for 3 h to remove the EDTA, cooled and finally reduced in H_2 flow at 140 °C for 2 h. Eight MSM samples under different pretreatment conditions were chosen as supports and the corresponding catalysts were named as Pd/T0-MSM, Pd/T1-MSM, Pd/T2-MSM, Pd/T3-MSM, Pd/T4-MSM, Pd/Ram-MSM, Pd/Rdw-MSM and Pd/Rnc-MSM.

2.3. Catalytic activity test

The hydrogenation of PS was carried out in a 500 mL agitated autoclave reactor. In a typical experiment, 2.0 g PS was firstly dissolved into a mixture of 10 mL tetrahydrofuran and 90 mL cyclohexane and then added in the reactor containing 0.5 g catalyst. Then the reactor was sealed and flushed with N_2 to remove the air and heated to 150 °C with agitation. After that, H_2 was introduced with the H_2 pressure of 5.0 MPa and the hydrogenation process was kept for 10 h. After reaction, the hydrogenated PS solution was centrifuged to separate the catalyst from the system. The final hydrogenated product was extracted with ethanol and then dried in a vacuum oven at 70 °C for 8 h.

2.4. Characterization

The morphology and structure of the particles were examined by scanning electron microscopy (SEM, FEI Quanta 200F, Holland) and transmission electron microscope (TEM, JEOM JEM 2100 LaB6, Japan) operated at 200 kV on a carbon-coated Cu grid. The BET surface areas and pore volumes of the samples were calculated by measuring N_2 adsorption-desorption isotherms using an ASAP 2020 instrument. Fourier transform infrared spectrophotometer (FTIR) spectra were collected on a Nexus 470 instrument (Nicolet, USA) over the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. Before the FTIR test, all the samples were dried in the oven (100 °C) overnight in order to avoid the water adsorption on the samples and all the characterizations were performed in the same conditions. The amount of surface silanol groups was determined by using titration method and the detailed information was provided in supplementary material. The crystal phases were determined by X-ray diffraction (XRD, X'Pert3 Powder, PANalytical, Holland) using Cu Kα radiation. The operation voltage and current was 45 kV and 40 mA, respectively. The scanning speed was set as 15°/min in the 2θ range of 10° to 90°. The concentration of aromatic rings was measured at 261.5 nm using a TU-1810 UV-VIS spectrophotometer (Pgeneral, China) and the calibration absorption curve was drawn with several PS solutions of known concentrations. So, the concentration of aromatic rings can be obtained by comparing the measured absorption and the calibration curve. The conversion of the aromatic rings, also called the degree of hydrogenation (HD) was calculated by $HD = 1 - C_A/C_{A0}$, where C_{A0} is the initial aromatic rings concentration and C_A is the concentration of aromatic rings after reaction.

3. Results and discussion

Fig. 1 and Fig. S1 display the SEM images of MSM with different steam treatment time. The microspheres with penetrating macropores on their surfaces can be clearly seen in Fig. S1 and the spherical morphology and macroporous structure are well maintained after the treatment even for 4 h. It is intriguing to find that the MSM has a relatively rough surface with some small particles attaching to it (Fig. 1 (0 h)), but the surface is gradually changed to smooth and clean with increasing the steam treatment time. The formation mechanism of macroporous shells in MSM has been well explained in our previous