



Fabrication of sulfonic acid modified mesoporous silica shells and their catalytic performance with dehydration reaction of D-xylose into furfural

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ABSTRACT

Sulfonic acid and aluminium modified mesoporous shell silica bead (MSHS, Mesoporous SHell Silica bead) were synthesized, respectively. Their catalytic performance was tested by dehydration reaction of D-xylose into furfural. Sulfonic acid modified MSHS showed higher selectivity of furfural than that of aluminosilicate MSHS. When aluminosilicate MSHS was used as catalyst, production of lyxose which is isomer of xylose was much more than using sulfonic acid modified MSHS. MSHS showed much more enhanced hydrothermal stability than other mesoporous silica materials, such as MCM-41.

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1. Introduction

Biomass can be obtained from agricultural waste, such as corn cobs, rice husk and bagasse, and is one of the most useful alternative raw materials for the synthesis of fine chemicals. Among them, furfural can be produced from D-xylose, which is an intermediate made from biomass. Furfural is not only valuable as a solvent but it is also a synthetic raw material for a range of furan chemical compounds [1,2]. It can also be used as a monomer for a range of polymers, such as polyester, polyimide, and polyurethane [3]. In a typical process, furfural is obtained by the dehydration reaction of D-xylose using acid catalysts (Fig. 1) [4–6], such as hydrochloric acid, sulfuric acid and acetic acid. This process causes corrosion of the reactor and environmental problems, which can result from the large quantity of waste water needed to dilute the strong acid [7]. For this reason, many research groups have focused on a solution with mesoporous solid catalysts being strong candidates. Since representative mesoporous silica, such as MCM-41 [8,9] and MCM-48 [10], were introduced by Mobil researchers in 1992, similar materials, including MSU [11,12], SBA-15 [13] and HMS [14], which have different pore sizes and structures, have also been reported. They have attracted considerable attention owing to their large surface area, void pore volume and uniform porosity. Their properties can lead to applications as

molecular sieves, catalysts, biosynthesis and templates for other porous materials. In particular, in the field of catalysis, they can be used as a support material for organic catalysts or nano-sized metal and metal oxide catalysts in a variety of reaction systems. They appear to be excellent materials for catalysts but they are vulnerable to hydrothermal reactions. Although the stability has improved recently, it is still unsatisfactory. In this respect, core/shell structures can be a useful solution, which combine the merits of both sides and has synergetic effects. For example, in the solid silica core/porous silica shell structure, the silica core improves the thermal stability and the porous silica shell makes room for a reaction similar to mesoporous silica. Recently, Büchel et al. [15] synthesized submicrometer-sized silica particles with a solid silica core, 420 nm in diameter, and porous silica shell, approximately 75 nm in thickness, by sol-gel polymerization of TEOS and octadecyltrimethoxysilane (C₁₈TMS) as porogens. Moreover, several materials with similar structures [16,17] were synthesized. The new catalytic system was expected to be used instead of the existing materials but there are no reports on their applications to catalysis.

This paper reports two different solid acid catalysts that consist of a dense silica core and mesoporous silica shell, which is based on the method reported by Büchel et al. [15]. One is functionalized with sulfonic acids as a Brønsted acid and the other with aluminium sites as a Lewis acid similar to zeolites. The catalytic performance of these materials was tested with a synthetic reaction of furfural using the dehydration of D-xylose.

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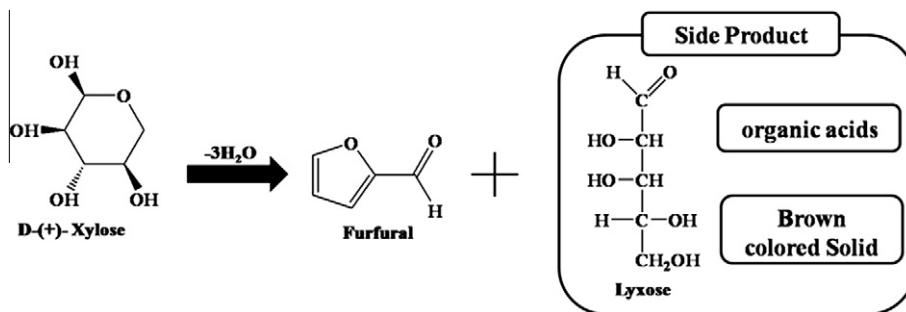


Fig. 1. Schematic reaction mechanism and side products of the dehydration of D-xylose into furfural.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%), hexadecyltrimethoxysilane (C₁₆TMS), 3-(mercaptopropyl) trimethoxysilane (3-MPTMS, 95%), aluminium isopropoxide (Al(C₃H₇O)₃) ammonium hydroxide (NH₄OH) solution were purchased from Sigma–Aldrich. 1,3,5-Trimethylbenzene (98%) was purchased from TCI. Other materials unless specified were reagent grade and distilled water were used in the preparation of aqueous solution.

2.2. Synthesis of mesoporous shell silica bead (MSHS)

MSHS was synthesized by the method reported previously [17]. Briefly, in a typical synthetic method of solid silica bead as a core, the solution was prepared by mixing 3.4 mL of NH₄OH solution, 74 mL of ethanol and 10 mL of deionized water. And then, 6 mL of TEOS was added slowly to the prepared solution under stirring for 1 h at room temperature. It is observed that solid silica bead was formed by changing color to white after around 10 min. To coat mesoporous shell on solid silica bead, 5 mL of TEOS and 2 mL of C₁₆TMS was added to the core solution and stirred for 1 h. The final solution was centrifuged at 6000 rpm for 20 min and removed the surfactant by washing with ethanol. The solid MSHS was dried at room temperature overnight and calcined at 550 °C for 6 h under air atmosphere to remove hexadecyl group. The reaction molar ratio was 11.4SiO₂:6NH₄OH:1C₁₆TMS:149H₂O:249.5 ethanol [17].

2.3. Synthesis of thiol group functionalized MSHS (MSHS-SH)

Pre-dried MSHS (3 g) under vacuum at 150 °C for 2 h was added to a solution of 11.7 mL of 3-MPTMS and 10 ml of solvent (xylene, mesitylene or triethylbenzene). The solution was refluxed for 12 h, cooled to room temperature, filtered, washed with *n*-hexane and dried [18] (Fig. 2).

2.4. Synthesis of sulfonic acid functionalized MSHS (MSHS-SO₃H)

MSHS-SH (3 g) was added to 300 mL of 0.1 M H₂SO₄ solution (1.0 wt.-%: MSHS-SH/H₂SO₄) and stirred for 4 h at room tempera-

ture. The solution was filtered and obtained solid was washed with excess deionized water and ethanol. The solid was dried at 60 °C in convection oven overnight. The final solid is MSHS-SO₃H which is sulfonic acid functionalized structure of MSHS [18] (Fig. 2).

2.5. Synthesis of aluminosilicate MSHS (MSHS-Al)

The synthetic method was similar to the method of MSHS. In a typical procedure, NH₄OH solution (3.14 mL), ethanol (74 mL), and deionized water (10 mL) mixed into a reactor and stirred for 30 min. TEOS (6 mL) was added to the solution and stirred for 1 h. Then, additional TEOS (5 mL) and C₁₈TMS (2.64 mL) were added to a solution and stirred. After 5 min, 3 mL deionized water solution which contained 0.96 g Al(C₃H₇O)₃ was dropped into the solution and stirred for 3 h. The product was retrieved by centrifugation at 3800 rpm for 30 min. Retrieved sample was dried at room temperature in a fumed hood overnight. To remove octadecyl group, calcinations had proceeded under air condition at 550 °C for 6 h.

2.6. Characterization

Nitrogen sorption isotherms were measured by an automatic adsorption instrument, Quantachrome Autosorb-1 (Quantachrome Corporation). Surface area was calculated by BET (Branauer–Emmet–Teller) method. Pore volume and size were calculated by BJH (Barrett–Joyner–Halenda) method. In the degassing port of adsorption analyzer for their pretreatments, MSHS and aluminosilicate MSHS were analyzed at 300 °C for 6 h whereas MSHS-SH and MSHS-SO₃H were analyzed at 60 °C overnight. TEM (Transmission Electron Microscope) images were taken using an FEI Morgagni™ electron microscope operated at an acceleration voltage of 300 kV.

2.7. Catalytic performance

Prepared catalysts were tested by batch reaction. In a standard method, D-xylose (0.9 g) and deionized water (30 mL) as a solvent were added into an autoclave equipped thermo controller. Catalytic reaction was performed at 170 °C for 1 h. Then the autoclave was cooled to room temperature with ice bath. Separation of catalysts and products was performed by centrifugation at 3800 rpm

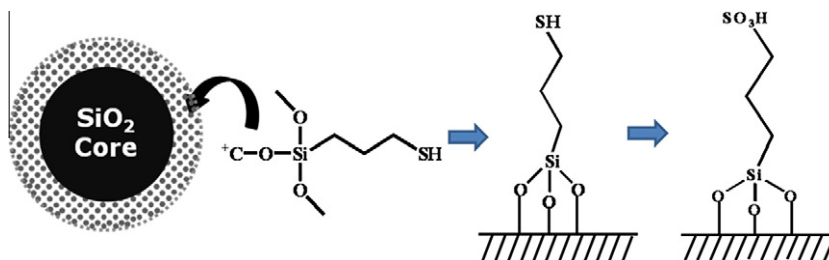


Fig. 2. Reaction scheme of MSHS-SO₃H and aluminosilicate MSHS.

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