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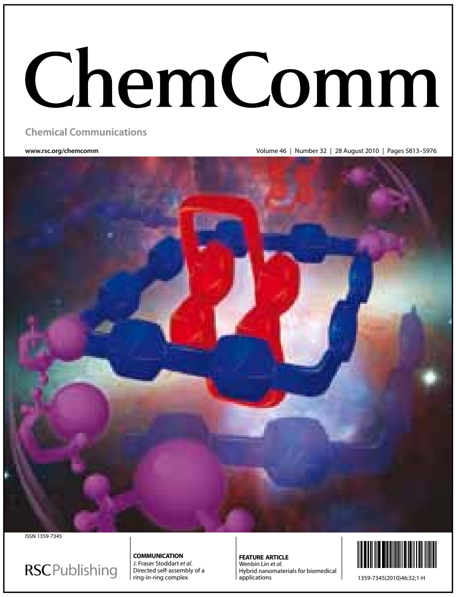

ChemComm

Chemical Communications

www.rsc.org/chemcomm Volume 46 | Number 32 | 28 August 2010 | Pages 5813–5976

ISSN 1359-7345

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COMMUNICATIONS

An efficient and reusable "hairy" particle acid catalyst for the synthesis of 5-hydroxymethylfurfural from dehydration of fructose in water

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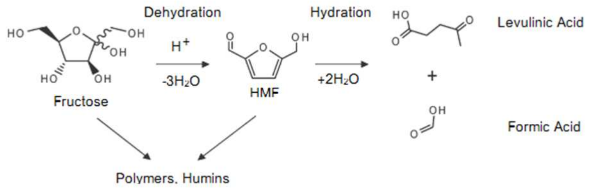
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Poly(4-styrenesulfonic acid) brush-grafted silica particles, synthesized by surface-initiated atom transfer radical polymerization, were employed as a reusable acid catalyst for fructose dehydration to 5-hydroxymethylfurfural (HMF) in water. The particles exhibited a high activity with the HMF yield up to 31%, in contrast to 26% from the corresponding free homopolymer catalyst.

Renewable biomass resources are promising alternatives for the sustainable supply of liquid fuels and chemical intermediates. As one of top building-block chemicals derived from biomass, 5-hydroxymethylfurfural (HMF) is a versatile intermediate for fine chemicals, pharmaceuticals, plastic resins, fuels, *etc.*[1,2] HMF is usually made from fructose by acid-catalyzed dehydration reaction.[3-5] From an environmental and economical point of view, although soluble small molecule acids are inexpensive and highly active catalysts for dehydration reactions, heterogeneous solid acid catalysts are more desired because of their facile recovery and lower adverse impacts to environment. As shown in previous studies, high HMF yields can be obtained in some organic solvents (e.g., dimethylsulfoxide) and ionic liquids.[5,6] However, these systems have some drawbacks in terms of high separation and recycling costs, and are generally not environmentally friendly.[7] Because of the low cost and the low toxicity, aqueous systems have attracted increasing attention for HMF preparation.

Unfortunately, previous work reported that the dehydration of fructose in aqueous media is generally nonselective, leading to many by-products such as insoluble humins.[7] Note that water is a product in the dehydration of fructose to HMF, and also a reactant in the further hydration of HMF (Scheme 1).[8] To enhance the selectivity and to facilitate the extraction of HMF, aqueous/organic biphasic systems were employed recently.[9]



Scheme 1. A typical reaction scheme for HMF production from fructose.

On the other hand, increasing materials' hydrophobicity has been demonstrated to be an effective method for enhancing catalysts' properties to promote organic reactions in water.[10,11] Because the surface hydrophobicity of inorganic materials can be readily modified by introducing organic moieties, hybrid organic–inorganic mesoporous materials have attracted considerable interest in the past few years.[12,13] These materials combine the advantages of both organic and inorganic components introduced into the mesoporous solids, exhibiting improved properties compared with either the wholly organic or inorganic materials. The observed higher activities of these catalysts have been attributed to the increased hydrophobicity near catalytic sites and the enhanced diffusion of organic reactants and products within the hydrophobic mesopores.

However, when a high content of organic catalytic groups is demanded, an important limitation for mesoporous materials is the surface saturation by small organic species. To overcome this constraint, herein we report the synthesis of a "hairy" particle acid catalyst by growing outward from the surface of silica particles poly(sodium 4-styrenesulfonate) brushes, which can be easily acidified to poly(4-styrenesulfonic acid) (PSSH) brushes, and the use of PSSH hairy particles as a recyclable acid catalyst for the dehydration of fructose to HMF in water (Scheme 2). Polymer brushes are a dynamic system possessing a certain degree of mobility.[14,15] The grafted linear PSSH chains take on extended conformations in water, due to their hydrophilic nature, and hence have increased interactions with fructose. Thus, polymer brush-supported acid catalysts resemble linear soluble polymer-supported catalysts. The increased mobility, compared with insoluble crosslinked polymer-supported catalysts, would improve the catalyst's performance. On the other hand, a unique microenvironment surrounding catalytic sites, i.e., sulfonic acid, is created by the hydrophobic polymer backbone, which to some degree mimics the characteristics of organic solvents and thus would facilitate the diffusion of organic reactants to the hydrophilic catalytic sites. When fructose molecules diffuse into the polymer brush layer of hairy particles, they experience a microenvironment of highly concentrated, hydrated acid groups attached to the hydrophobic polystyrene backbone, different from bulk aqueous phase, leading to the catalytic formation of HMF. In addition, the hairy particle acid catalyst can be separated from products after reaction, e.g., by centrifugation, and can be reused. This resembles cross-linked polymer-supported catalysts.

The poly(sodium 4-styrenesulfonate) brush-grafted silica particles were prepared by surface-initiated atom transfer radical

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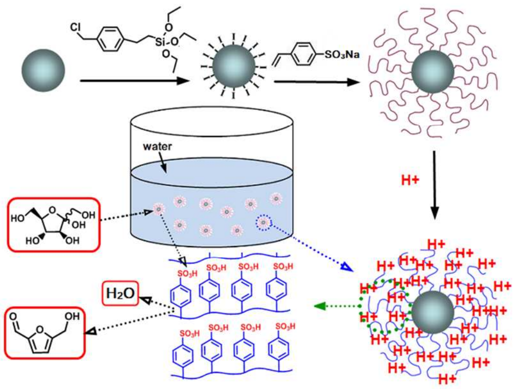

Scheme 2. Schematic illustration for the synthesis of poly(4-styrenesulfonic acid) brush-grafted silica particles and the dehydration of fructose to HMF catalyzed by the "hairy" particle acid catalyst.

polymerization (ATRP) of sodium 4-styrenesulfonate from ATRP-initiator-functionalized silica particles. ATRP is a versatile "living"/controlled radical polymerization technique.[16] The bare silica particles with an average size of 175 nm (Figure 1a), made by the Stöber process, were used in the present work. An ATRP initiator-terminated triethoxysilane, 2-[4-(chloromethyl)phenyl]-ethyltriethoxysilane, was immobilized onto the surface of silica particles via an ammonia-catalyzed hydrolysis and condensation process in ethanol.[17] Note that the use of a benzyl chloride initiator-terminated triethoxysilane yielded a linkage that contained only carbon-carbon bonds between the surface of silica particles and the polymer brushes, rendering the grafted polymer chains stable under the acidic conditions at elevated temperatures. The particle catalyst thus can be recycled multiple times without any significant change. The surface-initiated ATRP of sodium 4-styrenesulfonate from the initiator particles was carried out in a mixed solvent of methanol and water with a weight ratio of 1:3.5 at 75 °C using CuCl/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine as catalyst in the presence of a free initiator, benzyl chloride. The polymerization was monitored by ^{1}H NMR spectroscopy and was stopped after the monomer conversion reached 100%. The hairy particles were isolated and redispersed in acidic water with pH of ~ 1 and centrifugated again. This washing process was repeated additional five times, followed by drying of the PSSH hairy particles under high vacuum at 50 °C overnight. The degree of polymerization (DP) of the free polymer formed from the free initiator was 309, calculated from the monomer conversion and the monomer-to-initiator ratio.[15]

Transmission electron microscopy (TEM) image analysis provided direct evidence for the successful growth of polymer brushes on silica particles (Figure 1a-c). The polymer brush layer in the PSSH hairy particles can be clearly seen from Figure 1c. Compared with bare and initiator particles, there was a noticeable increase in the distance between adjacent silica particle cores. Thermogravimetric analysis (TGA) revealed that the weight retentions at 800 °C of initiator particles and PSSH hairy particles were significantly different (Figure 1d). If the weight retention difference at 100 °C between initiator particles and hairy particles is taken into consideration, the polymer content of hairy particles was 36.6 wt% (see the supporting information). Using the TGA data, the DP of the free polymer, and the size of bare particles, we calculated the grafting density of PSSH brushes, and it was 0.40 chains/nm^2. Additionally, the FTIR spectrum of hairy particles showed new bands at 1415, 1125 and 1010 cm^{-1}, which are assigned to the stretching vibrations of sulfonic acid groups (Figure S2).[9,18] Detailed synthetic procedures and characterization data can be found in the supporting information.

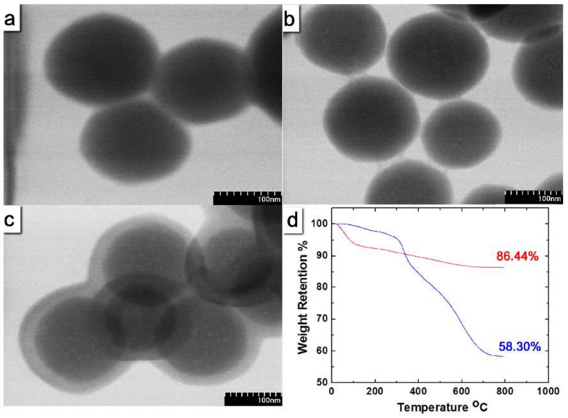

Figure 1. Transmission electron microscopy images of (a) bare silica particles, (b) initiator particles, (c) poly(4-styrenesulfonic acid) (PSSH) brush-grafted silica particles, and (d) thermogavimetric analysis (TGA) of initiator particles (red line) and PSSH-grafted particles (blue line). TGA was performed in air at a heating rate of 20 °C/min.

The catalytic performance of the hairy particle acid catalyst for the dehydration of fructose to HMF in water was examined. A typical condition is as follows. PSSH-grafted particles (0.10 g), fructose (0.23 g), and distilled water (3.5 mL) were added into a flask, which was then placed in a 120 °C oil bath. The effects of reaction time on the fructose conversion and the HMF yield were investigated by HPLC and the results are shown in Figure 2a. The conversion of fructose reached 80% at 6 h and the HMF yield was 27%. With increasing the reaction time, the fructose conversion and the HMF yield slowly climbed to ~ 91% and 31%, respectively, and then levelled off. Generally, a further increase in reaction time decreases the HMF selectivity due to its secondary reactions involving the hydration to levulinic acid and the formation of polymers and humins (Scheme 1). Interestingly, the reaction time had little effect on the HMF selectivity in this catalytic system, indicating that the further hydration reaction of HMF was restrained (Figure S3). For comparison, the homopolymer analogue, PSSH obtained from the free polymer formed in the synthesis of hairy particles by dialysis against pH 1.0 water, was also tested for the dehydration of fructose to HMF under the same conditions. The same amount of the homopolymer catalyst (36.6 mg) was used for the reaction based on the polymer content of the hairy particle catalyst. Intriguingly, the PSSH hairy particles always displayed a higher activity than the free homopolymer at the tested reaction times (Figure 2a). The highest HMF yields for the hairy particle catalyst and the homopolymer were 31% and 26%, respectively. This difference is likely due to the favourable microenvironment formed by the polymer brush architecture for the dehydration reaction.

We then studied the reusability of the hairy particle acid catalyst through five repeated dehydration reactions at 120 °C for 6 h under the same conditions. After each round of experiment,

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the HMF yield was measured and the hairy particles were isolated by centrifugation, purified, and reused. The results, shown in Figure 2b, indicated that this catalyst exhibited an excellent stability for the fructose conversion into HMF. After being used five times at 120 °C for 6 h, the HMF yield was still at ~ 24 %, though a slight decrease was observed. The slight decrease in the HMF yield might be caused by the particle loss in each round of separation and purification or as suggested in the literature by the possible unstability of Si–O–Si bonds between the grafted polymer and the particles under the acidic condition.[19]

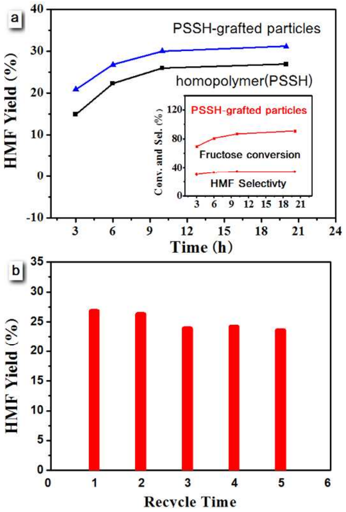

Figure 2. (a) Effect of reaction time on the fructose conversion to HMF catalyzed by PSSH-grafted silica particles and the homopolymer PSSH at 120 °C. The inset illustrates the effect of reaction time on the fructose conversion and HMF selectivity catalyzed by PSSH hairy particles at 120 °C. (b) Catalytic activity of the recycled PSSH-grafted silica particles for HMF production from fructose at 120 °C for 6 h.

Our hairy particle catalyst was more efficient for the synthesis of HMF from fructose when compared with commercial solid acids, such as Nafion NR50 and Amberlyst-15 which gave HMF yields of < 5 % under the same conditions. Unlike commercial solid acids that usually have rigid, crosslinked microstructures and are insoluble in water, PSSH brush-grafted particles can be easily dispersed in water, which maximizes the interactions between acid groups and fructose. The catalyst's brush structure, with extended conformations assumed by the PSSH chains densely grafted on silica particles, provides a unique solvation environment for enhancing the diffusion of organic reactants to the hydrophilic catalytic sites and catalysing the dehydration of fructose. Note that the acid brush layer of hairy particles can be finely tuned in terms of chain length, polymer architecture, grafting density, and the density of catalytic groups, which can be optimized to further improve the catalyst's performance.

In summary, PSSH brush-grafted silica particles were successfully synthesized through surface-initiated ATRP and subsequent acidification. These hairy particles were an efficient acid catalyst for the fructose dehydration to HMF in water, and were found to give a better HMF yield than the corresponding free homopolymer under the same conditions. We believe that the unique solvation microenvironment created by the densely grafted PSSH chains on the silica particles is responsible for the observation. The catalyst was reused multiple times with little decrease in the HMF yield. These hairy particles represent a promising approach toward high performance recyclable acid catalysts for the HMF synthesis in H_2O from renewable biomass.

The research was supported financially by the Divisions of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, US Department of Energy, and NSF (DMR-1007986, B.Z.). CCT and YLG also thank the National Basic Research Program of China (2010CB732300) and 111 Project (B08021).

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† Electronic Supplementary Information (ESI) available: Experimental section and Figures S1 and S2.

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