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Arylsulfonic acid functionalized hollow mesoporous carbon spheres for efficient conversion of levulinic acid or furfuryl alcohol to ethyl levulinate

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ABSTRACT

A series of arylsulfonic acid functionalized hollow mesoporous carbon spheres ($ArSO_3H$-HMCSs) with controllable $ArSO_3H$ loadings (1.8 and 3.2 wt%) and inner diameters (120–260 nm) were successfully prepared by chemical bonding $ArSO_3H$ groups to furfuryl alcohol-derived hollow mesoporous carbon spheres *via* diazonium coupling. The morphology, textural properties and chemical structure of as-prepared $ArSO_3H$-HMCSs were well characterized by TEM, FESEM, nitrogen gas porosimetry measurement, XRD measurement, Raman scattering and FT-IR spectroscopy as well as XPS surface probe technique. As the novel solid acid catalysts, the catalytic activity and stability of the $ArSO_3H$-HMCSs were evaluated by synthesis of ethyl levulinate from biomass-derived platform molecules, levulinic acid or furfuryl alcohol. The obtained excellent acid catalytic activity in comparison of other carbon-based $-SO_3H$ catalysts such as $ArSO_3H$-functionalized ordered mesoporous carbon, sulfonated hollow mesoporous carbon spheres as well as sulfonated incompletely carbonized D-glucose and cellulose was explained in terms of their strong Brønsted acidity and perfect hollow nanospherical morphology with thin mesoporous shell.

1. Introduction

Efficient conversion of inexpensive and renewable biomass to industrially important chemicals is one of the most popular topics in green chemistry [1–8]. Homogeneous Brønsted acids such as H_2SO_4, HF and benzene sulfonic acid are essential catalysts for the above processes. Nevertheless, the use of these acids has drawbacks such as corrosion, difficulty in the separation of products and catalysts, acid-waste generation, environmental pollution and added extra cost [6,9]. It is one of the key technologies to establish environmentally-friendly approaches for the biomass conversion-related processes by designing efficient, separable, recyclable and low-cost solid acid catalysts [10,11].

Recently, sulfonic acid functionalized carbon-based solid acids have attracted particular attentions in environmentally benign biomass conversion processes. The materials can be easily prepared by incomplete carbonization of cheap sulfopolycyclic aromatic compounds in *conc.* H_2SO_4 or sulfonation of incompletely carbonized natural organic matter (*e.g.*, D-glucose, sucrose, cellulose and starch) [12–14]. Owing to strong Brønsted acidity and high density, these amorphous carbon materials bearing $-SO_3H$, —COOH and —OH groups function as the efficient solid acid catalysts for various acid-catalyzed reactions such as esterification, transesterification, hydration, and hydrolysis [12,13,15–18]. However, owing to the nonporous structure, bulk carbon-based $-SO_3H$ catalysts generally have very small BET surface area (less than 5 $m^2\ g^{-1}$) [13], which limits their catalytic activity due to disadvantages of lack of acid site numbers, poor accessibility of the acid sites as well as slow mass-transport rate. The problems are expected to be ameliorated by adjusting the morphological and textural properties of sulfonic acid functionalized carbon-based solid acids, which can influence the active site numbers, the accessibility of active sites on the catalyst surface and inside the pores to the substrates as well as mass-transport of the reactant or product molecules [19–24].

Motivated by the aforementioned ideas, in the present work, a series of novel carbon-based $ArSO_3H$ catalysts ($ArSO_3H$-HMCSs) with hollow mesoporous spherical morphologies and controllable $ArSO_3H$ loadings as well as inner diameters were successfully prepared by chemical bonding arylsulfonic acid groups to furfuryl alcohol-derived hollow mesoporous carbon spheres (HMCSs) *via*

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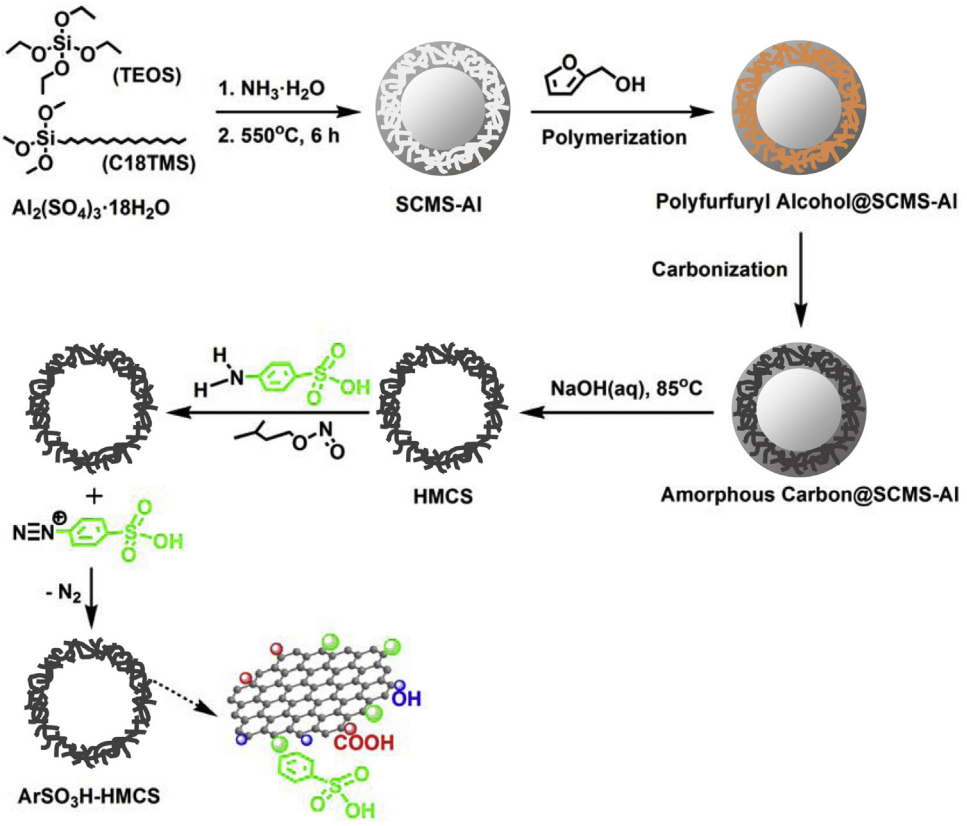

Scheme 1. Route of preparation of $ArSO_3H$-HMCSs materials.

diazonium coupling (Scheme 1). Hollow nanosphere catalysts with outstanding properties including hollow interiors, permeable and thin shells, shortened diffusion distance as well as unique textural properties (*e.g.*, very large BET surface area and porous structure) may significantly improve the accessibility of the active sites to the substrates, and thereby the enhanced catalytic activity of carbon-based —SO_3H catalysts in various chemical transformations is expected to be obtained.

To evaluate the heterogeneous acid catalytic performance of the $ArSO_3H$-HMCSs, synthesis of ethyl levulinate from esterification of levulinic acid and alcoholysis of furfuryl alcohol were selected as the model reactions. Ethyl levulinate is a member of alkyl levulinates family that is versatile chemical feedstocks with numerous applications in flavoring and fragrance industry or as a blending component in biodiesel [25,26]. The threat of an oil shortage is stimulating the search for alternative feedstocks to chemicals, and therefore, efficient conversion of biomass-derived levulinic acid or furfuryl alcohol to levulinate esters has attracted especial interests. For direct esterification of levulinic acid to produce levulinate esters, the byproduct water may inhibit the reaction to proceed effectively. An atom-economic and convenient method for the synthesis of alkyl levulinates can be envisioned by alcoholysis of furfuryl alcohol. For the aforementioned two reactions, development of efficient, separable and recyclable solid acid catalysts is the most important issue to establish environmentally sustainable approaches. Conventional solid acid catalysts including macroporous ion-exchange resins (*e.g.*, Amberlyst-15 or -70) [27,28], microporous zeolites (*e.g.*, HZSM-5) [29,30], mesoporous aluminosilicates (*e.g.*, Al-TUD-**1**) [31], sulfated metal oxides (*e.g.*, SO_4^{2-}/TiO_2 and SO_4^{2-}/ZrO_2) [28] and sulfonic acid-grafted silica (*e.g.*, SO_3H-SBA-15) [29,32] have been employed in synthesis of levulinate esters by esterification and ethanolysis reactions. However, the moderate yields of levulinate esters were obtained; additionally, catalyst deactivation was observed during recycling the solid acids.

To further evaluate the heterogeneous acid catalytic activity per acid site of the $ArSO_3H$-HMCSs, the reference acid catalysts including commercial Amberlyst-15, homogeneous benzene sulfonic acid and sulfuric acid as well as other SO_3H-functionalizd carbon-based materials like arylsulfonic acid functionalized ordered mesoporous carbon ($ArSO_3H$-OMC), sulfonated HMCSs (SO_3H-HMCSs) and cellulose- or D-glucose-derived carbon solid acid (SO_3H-CC or SO_3H-GC) prepared by partial carbonization of a microcrystalline cellulose powder or D-glucose and then sulfonation of the resulting carbon precursor in *conc.* H_2SO_4, respectively, were also tested. Additionally, influence of $ArSO_3H$ loadings and inner diameters of the hollow spherical $ArSO_3H$-HMCSs on the catalytic activity was studied. Based on the above results, influence of morphological and textural properties on the heterogeneous acid catalytic activity of carbon-based —SO_3H catalysts was revealed.

2. Experimental

2.1. Materials

Furfuryl alcohol (98%), sulfanilic acid (99%) and tetraethylorthosilicate (TEOS, 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Octadecyltrimethoxysilane (C18TMS, 98%) was purchased from TCI. Isopentyl nitrite (96%) and levulinic acid (98%) were purchased from Sigma–Aldrich. Commercial Amberlyst-15 was purchased from Alfa Aesar. All other chemicals were analytical grade, and they were purchased from Beijing Fine Chemical Co. (China).