

Short Communication

Debenzylation of vanillic acid over sulfosuccinic acid functionalized mesoporous silica nanocomposites

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ABSTRACT

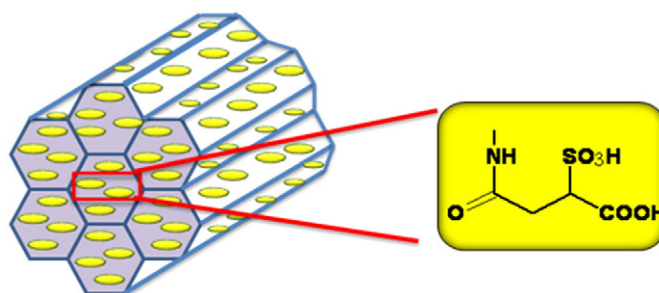
Sulfosuccinic acid functionalized mesoporous silica (SBA/SSA) was synthesized and characterized for debenzoylation of vanillic acid in liquid phase for the first time. The catalytic activity studies showed high activity (82%) and selectivity (96%) for the desired product vanillic acid over SBA/SSA compared to 74% selectivity over silica/SSA. Synergistic effects of acidic/basic groups responsible for higher activity and selectivity were explained with plausible mechanism.

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1. Introduction

The discovery of ordered mesoporous materials (OMS) has opened new avenues to incorporate a wide variety of functional groups because of their outstanding properties such as high surface area, uniform and tunable pore diameter, pore volume and easy diffusion. Unique properties of these OMS have encouraged the organic tailoring of the mesoporous surface for advanced applications in the field of ion-exchange, adsorption and catalysis [1,2]. Therefore organic moieties can easily be functionalized to achieve acidic, basic or bifunctional properties via different synthetic techniques [3]. Microporous materials such as zeolites [4] and sulphonated acid catalysts like Amberlyst-15 and Nafion-H were successfully exploited for many significant catalytic applications [5,6]; however, the smaller size of zeolite materials and diffusional difficulties limit their practical utilization to incorporate larger organic moieties. The stringent environmental regulations also forced the modern chemical industry to seek for the development of new heterogeneous systems for easier product recovery, regeneration of the catalytic active sites and to overcome effluent treatment problems. One such problem has been associated with debenzoylation of aromatic benzyl ether (especially for de-protection reaction) for which harsh and toxic chemicals are still in use for many substrates. Benzoylation of phenols is required for selectively protecting the –OH group which is more accessible to react and form side products during any reaction. However at the end of the reaction debenzoylation is done for regenerating the phenolic group. Although various methods have been

employed, catalytic hydrogenolysis (H₂ in the presence of Pd/C or Raney Ni) is commonly employed deprotection method wherein the pyrophoric nature of the reaction limits their versatile use [7,8]. Moreover the procedure is tedious, costly and the deprotection procedure is not compatible with other functional groups. Silica supported sodium hydrogen sulfate [9,10], trifluoroacetic acid [11] and solid supported acid catalyst [12] have already been reported for debenzoylation reactions. Several researchers have incorporated stronger acid ligands such as propylsulfonic acid, benzenesulfonic acid [13,14] via co-condensation method into the mesoporous framework but not much effort were paid to develop mild and bifunctional acid nanocomposites. The synergistic effects (acid–base co-operation or the bifunctional catalysis) are very common in biological catalytic systems but the cooperative effect of –NH– and sulfonic groups fused together on mesoporous framework for deprotection of benzyl ethers has not been explored. Many heterogeneous catalysts [15] were reported for the deprotection of benzyl ethers but according to the literature, no report is available yet for



Scheme 1. Schematic presentation of SBA/SSA synthesis.

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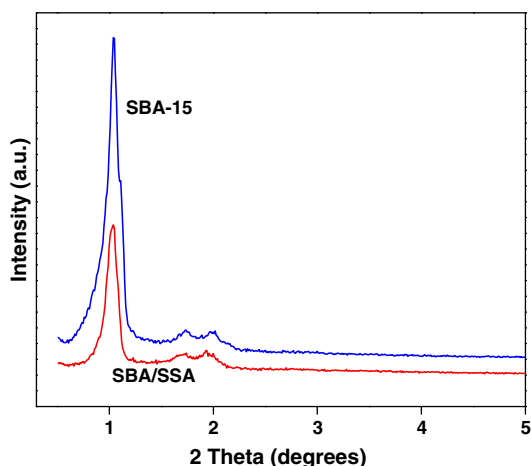


Fig. 1. PXRD pattern of SBA-15 and SBA/SSA catalysts.

Table 1
Structural parameters of different catalysts.

Materials	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
SBA-15	653	0.93	8.4
SBA-APTS	152	0.29	6.2
SBA/SSA	80	0.168	5.4

debenzylation of vanillic acid over functionalized SBAn materials. With this view, we report synthesis and characterization of bi-functionalized SBA/SSA nanocomposites by covalently linking carboxylic acid groups into the SBA-15 framework which resulted in a continuous pattern of their linkage i.e. –NH– and sulfonic acid groups for this interesting conversion.

2. Experimental

2.1. Synthesis of SBA/SSA catalyst

The synthesis of SBA-15 was carried out in accordance to the earlier reports using Pluronic (P123) (EO₂₀PO₇₀EO₂₀, MW = 5800, Aldrich) as surfactant and TEOS as the silica source [16]. Typically, to 1 g of SBA-15, 10 ml of aminopropyltriethoxysilane (APTS) was stirred in dry toluene (20 ml) under inert atmosphere (Scheme 1). The product SBA/APTS was filtered, washed exhaustively with ethanol in Soxhlet extractor for 24 h and dried under vacuum. For the functionalization of SBA/APTS with SSA, 1.5 ml of sulfosuccinic acid with 1.2 g of HOBt (1-Hydroxybenzotriazole) and 1.2 g of EDCI (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide) (acts as a carboxyl activating agent for coupling to primary amines) at 0 °C was stirred for half an hour. To this mixture, 1 g of SBA/APTS was added in stirring conditions at room temperature for 4 h. Finally the product was filtered and washed thoroughly with methanol and water (to remove the urea formed as a byproduct) to generate SBA/SSA nanocomposites. Ninhydrin test at room temperature (no coloration) confirms the completion of functionalization. Silica-SSA was synthesized exactly under the similar reaction conditions (APTS and SSA).

3. Results and discussions

Powder X-ray diffraction pattern (PXRD) of SBA/SSA samples (Fig. 1) at low angles showed peaks similar to the SBA-15 materials. The characteristic diffraction peaks at (100), (110) and (200) planes can be indexed to reflections comprising of two dimensional hexagonal p6mm symmetry indicating that the materials possess ordered

mesoporous structure [17]. However, a slight decrease in the intensity of the diffracted peaks for SBA/SSA compared to SBA-15 showed a partial loss of long range ordering due to incorporation of SSA inside the material. The nitrogen adsorption–desorption isotherm of SBA/SSA, SBA/APTS and SBA materials (Fig. S1) showed Type IV isotherm according to IUPAC classification with an H1 hysteresis loop indicative of the mesoporous nature of the sample, the hysteresis loop at relative pressure p/p_0 in the range of 0.4–0.5 is consistent and comparable to the original SBA-15 material [17]. Surface area, pore size and pore volume (Table 1) of SBA/SSA sample decreased after functionalization confirming the incorporation of sulfosuccinic acid inside the silica framework. The incorporation of sulfosuccinic acid was further confirmed by ¹³C NMR. The ¹³C spectrum (Fig. 2) showed four types of carbon. The presence of distinguished peak at 177 and 173 ppm for C1 and C2 carbon respectively indicates the distinct environment of the carbonyl (–CO) group present in sulfosuccinic acid [18]. Slightly higher δ value for C1 peak is observed due to the shielding effect of SO₃H group present in the vicinity to –COOH groups where as the lower value of C2 may be attributed to more electron density due to the amide linkage resulting in lowering of the chemical shift. Peaks at 64 and at 26 ppm are due to the presence of the methylene group (C3 and C4) in the SBA/SSA nanocomposites [19]. Three peaks at 41, 20 and 9 ppm indicate the presence of aminopropyl group attached to sulfosuccinic acid. Additionally the amount of sulfosuccinic acid within the mesopores of SBA-15 was estimated by EDXRF (Fig. 3). The amount of sulfur content (S K α counts indicates the amount of S present) in the SBA/SSA and silica-SSA (from CHN analysis) was found to be 0.218% and 0.27% respectively which is in agreement with the theoretical calculated values. The SEM images of SBA/SSA and silica-SSA (Fig. S3A) showed aggregation compared to SBA/SSA (Fig. S3B) wherein the mesoporous material retained the rod shaped geometry. In order to further confirm the incorporation of sulfosuccinic acid inside the porous framework, IR frequencies of SSA, SBA/APTS and SBA/SSA (Fig. 4) were compared. Shifting to lower values of OH stretching of SSA (3650 cm⁻¹) compared to SBA/SSA (3520 cm⁻¹) may be due to the intermolecular H-bonding between the groups (–COOH). Furthermore, broadening of the peak indicates the presence of N–H stretching for amide linkage in SBA/SSA. Also the N–H frequency is consistent with the SBA/APTS confirming the covalent binding of SSA to SBA-15 via APTS [20]. The peak at 1728 cm⁻¹ due to –CO– stretching in SBA/SSA is consistent with the SSA. Peak due to S–O stretching in SSA at 1380 cm⁻¹ has slightly

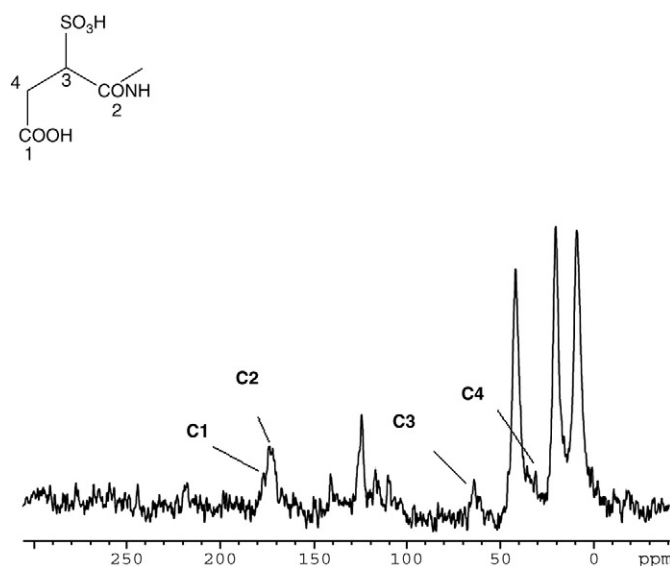


Fig. 2. ¹³C NMR of SBA/SSA catalyst.

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