



Stability and catalytic properties of porous acidic (organo)silica materials for conversion of carbohydrates



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ABSTRACT

Sulfonic acid-modified mesoporous SBA-15-type silica and hybrid organosilica catalysts were prepared using the co-condensation and grafting functionalization methods. The catalytic activity of these materials for fructose dehydration to 5-hydroxymethylfurfural was studied in aqueous medium and in DMSO. The prepared materials were characterized by XRD, SEM, elemental analysis, nitrogen physisorption and ^{29}Si CP MAS NMR. Special focus was on evaluating the influence of the structural modification of the mesoporous catalysts on their stability under the conditions of catalytic conversion of carbohydrates. In aqueous medium all catalysts show very low activity and HMF selectivity. However, when the reaction is carried out in DMSO, HMF yields of up to 88% can be achieved with a minimum amount of sulfonic acid-modified catalyst. Among the materials tested, the hybrid organosilica-based catalyst shows the highest dehydration rate. It is demonstrated that pure silica-based catalysts degrade strongly under the catalytic conditions. The hydrothermal stability of the mesoporous catalysts is improved in the presence of organic moieties in their structure. The co-condensed organic-inorganic catalysts retain much better the mesoporosity and are less susceptible to the loss of catalytic functional groups anchored to their surface compared to their pure silica counterparts. The methodology for the introduction of functional groups has also a profound impact on the catalyst stability. Species incorporated into the catalysts via the direct co-condensation method show much higher stability than those introduced via a post-synthetic grafting procedure.

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1. Introduction

Depleting fossil resources, as well as environmental concerns regarding their extraction and utilization, necessitate the development of new technologies based on more sustainable feedstock for the production of important chemical intermediates and fuel components. An important candidate to partly replace fossil feedstock is carbohydrate biomass because of its abundance, renewable nature and relatively uniform chemical composition facilitating its utilization in the chemical industry [1,2]. The transformation of the main constituents of carbohydrate biomass, cellulose and hemicellulose, to useful chemicals proceeds via specific key intermediates that are usually referred to as platform chemicals. A wide range of value-added chemicals can be obtained from these compounds. One of the most promising platform molecules is 5-hydroxymethylfurfural (HMF), which can serve as a precursor for monomers (e.g., furfuryldicarboxylic acid, FDCA) and fuel components [3,4].

The conversion of fructose to HMF is an important model reaction in carbohydrate chemistry. It can be promoted by different Brønsted and Lewis acidic catalysts [5,6]. For commercial applications, heterogeneous catalysts are generally preferred in view of easier separation and regeneration. Silica is among the most widely used carrier materials for heterogeneous catalysts due to its high mechanical and thermal stability [7] as well as the possibility to tune its chemical properties by the introduction of different functional groups [8].

Even without a catalyst, HMF can be obtained from fructose by high-temperature dehydration in ionic liquids [6] and in several other solvents such as DMSO [9–11]. The utilization of an acid catalyst allows performing the reaction at milder reaction conditions with high efficiency. However, from an environmental point of view water as a solvent is preferred. Fructose dehydration in aqueous media suffers from side reactions resulting in low yields of the desired HMF product [12].

Various solid acid catalysts and in particular organic acid-functionalized ordered mesoporous silica materials have been applied in a large number of acid-catalyzed reactions, such as condensation and acetalization reactions [13,14]. For the conversion of biomass-derived compounds, water is considered the preferred and “green” reaction medium. However, in aqueous environment

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the catalyst stability can be compromised due to hydrolysis of the active sites [15]. In order to increase the stability of these materials in the presence of water, specific microenvironments can be created inside their pores which suppress the decomposition of the (organo)silica material. Increased hydrophobicity of the pores may also decrease the local water concentration, thereby decreasing the tendency to form humins upon the conversion of carbohydrates, as well as increasing the material's resistance to hydrolysis and subsequent loss of functional groups.

Hydrophobicity can be conveniently controlled by introduction of stable organic bridging groups between the silicon moieties, creating a hydrophobic microenvironment inside the catalyst pores. Hybrid organic–inorganic periodic mesoporous organosilica (PMO) materials have gained significant attention for application in adsorption and membrane separations [16,17] as well as in catalysis [18]. Its synthesis involves the hydrolysis and template-assisted condensation of bis-(trialkoxysilane)-functionalized compounds, by which highly ordered materials can be obtained [19–21]. It has been suggested that the increased hydrophobicity leads to increased hydrothermal stability of the materials [19]. By optimizing the hydrophobicity of silane precursors, functionalized organosilica materials with enhanced hydrothermal stability can be obtained [19].

Catalytic functionalities can be introduced in (organo)silicas by either post-synthesis grafting on the porous material or co-condensation of a functionalized alkoxy silane with an (organo)silica precursor. [8] During grafting, the functionalized alkoxy silane reacts with the free surface silanol moieties. The nature and properties of the resulting grafted species depend on the concentration and distribution of surface silanol groups in the materials. Furthermore, one cannot exclude surface-condensation of the organosilane precursors on the catalyst surface resulting in the formation of a poorly defined amorphous agglomerates inside the catalyst pores. Co-condensation usually ensures a better anchoring and more homogeneous distribution of the introduced functional groups than grafting [22,23].

Recently, Dumesic et al. [15] demonstrated that co-condensed sulfonic acid-modified SBA-15 and ethene-bridged periodic mesoporous organosilica C–C-PMO and their admixtures can successfully be used as catalysts for the conversion of fructose to HMF in a fixed-bed reactor. However, it was found that under reaction conditions (THF/H₂O 4:1, *T* = 130 °C) functionalized groups were hydrolyzed and removed from the active catalyst. This raises questions on the suitability of such materials for application as catalysts for biomass conversion.

In this study, sulfonic acid-modified silica and organosilica catalysts were prepared. Preparation of the materials was performed by either grafting a sulfonic acid trialkoxysilane derivative onto prepared SBA-15 and C–C-PMO, or by co-condensation with either silica (TEOS) or ethane-bridged organosilica (bis-triethoxysilyl ethane, BTESE) precursors. The functional groups used in this study are shown in Fig. 1. The hydrothermal stability of the synthesized materials and their reactivity for fructose dehydration in water and DMSO were investigated. Special focus was on the analysis of the influence of the functionalization method and the nature of the support material on the catalyst stability.

2. Experimental

Fructose (99%, Sigma–Aldrich), DMSO (Sigma–Aldrich), TEOS (98%, Merck), bis(triethoxysilyl)ethane (BTESE, 99%, Sigma–Aldrich), Mercaptopropyltrimethoxysilane (MPTMS, 95%, Sigma–Aldrich), Phenyltriethoxysilane (PTES, 98%, Sigma–Aldrich), 2-(4-chlorosulfonylphenyl)-ethyltrimethoxysilane (CSPTMS, 50% solution in CH₂Cl₂, ABCR), Pluronic P123 (*M_n* ≈ 5800,

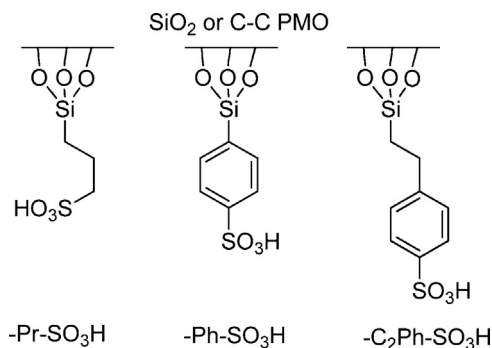


Fig. 1. Sulfonic acid groups used for functionalization of (organo)silica mesoporous materials.

Sigma–Aldrich), HCl (37% aqueous solution, BDH Prolabo), hydrogen peroxide (30 wt% aqueous solution, Sigma–Aldrich), chlorosulfonic acid (98%, Fluka) were used as received without further purification.

2.1. Materials synthesis

2.1.1. SBA-15 and C–C-bridged PMO

SBA-15. Synthesis of SBA-15 was performed according to established procedures [24,25]. To a stirred solution of Pluronic P123 (2 g) in aqueous HCl (75 mL, pH = 1.5), TMOS (3.3 g, 22 mmol) was added at 40 °C and the mixture was stirred for overnight. The mixture was then transferred to a Teflon-lined autoclave and aged at 100 °C for 24 h. After filtration, the solid was washed thoroughly with water and ethanol and dried in air. Detemplation of the material was performed by calcination at 550 °C for 8 h in static air.

C–C-Bridged PMO (C–C-PMO). For C–C-PMO, BTESE was added to a surfactant solution at 35 °C with a final synthesis ratio of 1 BTESE: 0.03 P123: 8.3 HCl: 318 H₂O: 5.33 n-BuOH. After stirring overnight at the same temperature, the mixture was aged for 48 h at 100 °C. The resulting material was washed thoroughly with water and ethanol and dried in air. Detemplation of the material was performed by Soxhlet-extraction with acetone overnight.

2.1.2. Co-condensation

General. In a typical synthesis P123 (2 g) was dissolved in 2 M aqueous HCl (62.5 g) at 40 °C. Then silica (TEOS) or organosilica (BTESE) precursor was added (18 mmol) and the mixture was allowed to prehydrolyze. Upon formation of a slightly blurry suspension, functionalized organosilane (PTES, MPTMS or CSPTMS, 2 mmol) was introduced to the mixture and stirred overnight at 40 °C. The mixture was then transferred to either a Teflon-lined autoclave or an autoclavable PP-bottle and kept statically in an oven at 100 °C for 48 h. After drying in air, the materials were detemplated by Soxhlet-extraction with acetone and dried in air.

Propylsulfonic acid-modified SBA-15 (SBA-Pr-coc) and -PMO (PMO-Pr-coc). Co-condensation was performed using MPTMS as the functionalized precursor. Oxidation of the surface mercaptopropyl groups to the corresponding propylsulfonic acid moiety was carried out in situ by adding 0.7 g of 30% aqueous H₂O₂ to the synthesis mixture.

Phenylsulfonic acid-modified SBA-15 (SBA-Ph-coc) and -PMO (PMO-Ph-coc). Co-condensation was performed using PTES as the functionalized precursor. Before sulfonation, the phenyl-functionalized material was dried in vacuo for 3 h at 100 °C. Sulfonation was carried out by suspending 1 g of dried material in dry CH₂Cl₂ (15 mL) at room temperature followed by the introduction of 5.2 mL of chlorosulfonic acid. The mixture was refluxed for 1 h and after cooling down quenched with glacial acetic acid.

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