

Mesoporous Materials-Based Catalysts for Chemical Hydrolysis of Polysaccharides

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Introduction

Solid-supported catalysts enable the replacement of solution-based catalytic chemical processes leading to facile separation of products from the reaction medium, fewer byproducts, lower energy consumption, and less environmental pollution. Recently, this catalytic method has received a lot of attention provided that it could apply to enhance the conversion of a variety of biopolymers into fuels. Cellulose is one of the biopolymers of interest given the large number of specialty chemicals and biofuels that could be synthesized using cellulose as a starting material. Cellulose consists of glucose units connected through β -1,4-glycosidic bonds. Hydrolysis of cellulosic polymers in the presence of strong acids results in oligosaccharides, glucose, and ultimately in specialty chemicals that are typically obtained from fossil fuels processing. Typical industrial workhorses industrially used in the hydrolysis of cellulose are hydrochloric acid (HCl) and sulfuric acid (H_2SO_4). There are a variety of problems created by strong acids, including difficult product separation, corrosion of reaction vessels, poor-to-none catalyst recyclability, and the need for waste treatment; therefore, catalysts that could avoid any of these or all are highly sought. Solid supported catalysis is viewed as solution to eliminating corrosion, the need for waste treatment and provide an excellent separation platform.

Conversion of Cellulose to Sugars and other Valuable Chemicals

As illustrated in Figure 1, the glucose is obtained by hydrolytic cleavage of the β -1,4-glycosidic bonds. Not showed in Figure 1, also, cellobiose, which is a disaccharide of glucose, is the repeating unit of the cellulose polymer.

Solid Supports for Catalyst Immobilization

Solid supported catalysts are obtained by immobilization of active catalytic groups onto the solid support surface. Immobilized catalysts are physically confined or localized, while retaining their catalytic activity, and can be used repeatedly and continuously. Among platforms for catalyst immobilization, porous materials stand out as they offer capability of protecting the catalytic unit from degradation. In this light, Mesoporous Silica Nanoparticles (MSNs) have attracted a much attention in the field of catalysis because of their high surface area and pore size tunability. Provided the nucleophilic nature of the silanol groups on the surface of MSNs enables their functionalization with a plethora of functional groups, via either post-synthetic grafting or by co-condensation [1,2]. Such groups serve either as catalysts or as linkers for covalent or electrostatic immobilization of catalyst to be hosted in pores. A large number of mesoporous silica nanospheres has been developed. Each group that made significant contributions to the field by enhancing the properties of the mesoporous silica (making a difference in particle size, porosity, pores arrangement etc.), has chosen names to describe material attributes or the group that has synthesized the material the first time.

In addition, carbon-based mesoporous supports have been synthesized by using mesoporous silica materials as sacrificial

template. Mbaraka et al. demonstrated sulfonic acid immobilization in HMS and SBA-15 by oxidation of a pre-anchored thiol functionality [3]. As illustrated in Figure 2, [4] the accessibility of the SH is critical to obtaining a uniform distribution of acid catalytic sites and further improve reaction kinetics. Recently, the Fukuoka group fabricated a Ru/CMK-3 catalyst by a conventional impregnation method using Ruthenium salts.

Mesoporous Solid Supported Catalysts for Cellulose Conversion

The scarcity of recyclable solid materials as a replacement of homogeneous acid catalysts is usually attributed to the low density and strength of the acid sites on their surface. Since the hydrolysis of cellulose is directly correlated to the concentration and pKa of the acid employed, efficient catalysts require a high density of accessible and strong Brønsted acid sites with high stability in aqueous environments. In the past few years, considerable progress has been made in the development of such catalysts, especially by employing porous platforms that offer the necessary high surface area to achieve the high density of catalytic sites [5].

Various solid acid catalysts such as heteropoly acids, sulfonated resins, sulfonated carbon, sulfonic acid functionalized silica, WO_3/ZrO_2 , Ru/CMK, ionic liquids, zirconium phosphate, hierarchical H-USY zeolites, sulfonated hierarchical H-USY zeolite, TiO_2 , Ti-MCM-41, have been tested for hemicellulose and/or cellulose hydrolysis. Yang et al. tested solid acid catalysts such as H-Beta, H-Y, and H-ZSM-5 to obtain HMF from glucose [6].

The Fukuoka group compared a Ru/CMK-1, Ru/XC-72 (carbon black), Ru/AC (activated carbon), and Ru/C60 were also used, to allow a comparison of the catalytic activities. Among these catalysts, Ru/CMK-3 had the highest cellulose conversion and glucose yield [7]. The ligno-cellulosic biomass-like agricultural residues and wood chips contain C6-sugars (e.g., D-fructose, D-glucose, and D-mannose), which are valuable precursors for numerous chemicals having valuable applications. As indicated in Figure 1, often the cellulose conversion to glucose is just a first step in obtaining other valuable chemicals.

The Katz's group demonstrated depolymerization of adsorbed (1 \rightarrow 4)- β -D-glucans (β -glu) derived from crystalline cellulose (*Avicel*), using weak-acid sites of postsynthetically surface-functionalized mesoporous

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carbon nanoparticle (MCN) catalysts HT₅-HSO₃-MCN and COOH-MCN and investigated the role of acid-site density and β-glu molecular weight on this depolymerization. Their study concludes that both HT₅-HSO₃-MCN and COOH-MCN hydrolyze adsorbed β-glu strands and afford glucose yields of 73% and 90%, respectively, at a buffered pH of 2.0 after 3 h treatment at 180°C. These yields are significantly higher than the 16% yield of an unfunctionalized MCN-control catalyst under otherwise identical conditions, demonstrating the importance of postsynthetic surface functionalization for achieving weak-acid catalytic hydrolysis [8].

The Sels group developed a new class of sulfonated silica/carbon nanocomposite catalysts, capable of achieving high glucose yields compared to reference catalysts and commercial zeolites. The organic part of the hybrid material not only generates flexibility and versatility for further functionalization with e.g., acid groups; its silica components also allow good mechanical and thermal stability. The nanocomposites were synthesized by the evaporation-induced

triconstituent co-assembly method in order to ensure high entanglement of carbon and silica. Tetraethyl orthosilicate (TEOS) is used as silica precursor, while Pluronic F127 triblock copolymer (EO₁₀₆PO₇₀EO, Mw=12600) acts as the structure-directing amphiphilic surfactant.

Sucrose was used also as a green alternative carbon source instead of the commonly reported phenol resins. Evaporation of the sucrose/silica/F127 solution, followed by carbonization in nitrogen atmosphere at 673 K or 823 K decomposes F127 and transforms the sucrose moieties into carbon residues, resulting in nanocomposites containing hydrophobic carbon in close contact with the stabilizing hydrophilic silica matrix [5]. Figure 3 shows a detailed analysis of several solid acid catalysts with the distribution of cellulose hydrolysis products. Bokade's group is targeting furanics like 2,5-dimethylfuran and 5-hydroxymethylfurfural (5-HMF). Of these, particularly 5-HMF is currently receiving a great deal of attention. 5-HMF can be converted to a range of derivatives having potential applications in the biofuels (furanics), polymer, and solvent industries. The group reported the use of H-ZSM-5 with Si/Al ratio 37 along with the bimodal micro/mesoporous H-ZSM-5 (Bimodal-HZ-5) [6].

As showed in Figure 4, the results if this studies indicate that a distribution of products are yielded, suggesting the potential for enhancing selectivity of these catalysts. Fu's group experiments on the hydrolysis of cellobiose with Fe₃O₄-SBA-SO₃H (Figure 5) showed that the magnetic solid acids greater performance than sulfuric acid. The magnetic solid acid contains concentrated acid sites and the uniform channels allow the reactants to easily enter and interact with these

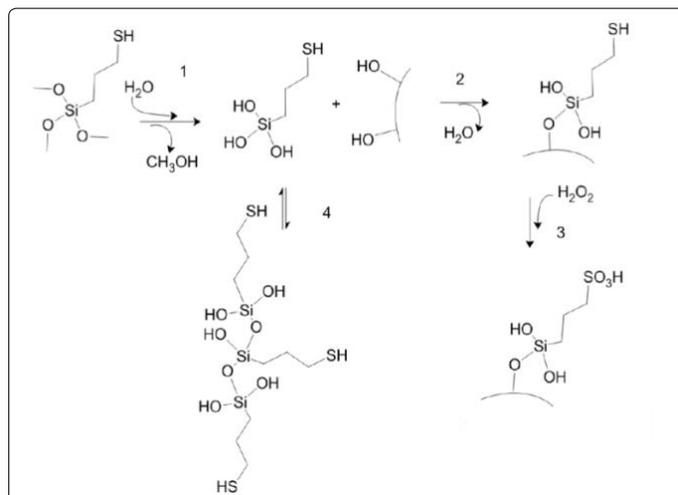


Figure 2: Schematic representation of the Sulfonic Acid Synthesis for any silica-supported thiol (Adapted from ref. [4]).

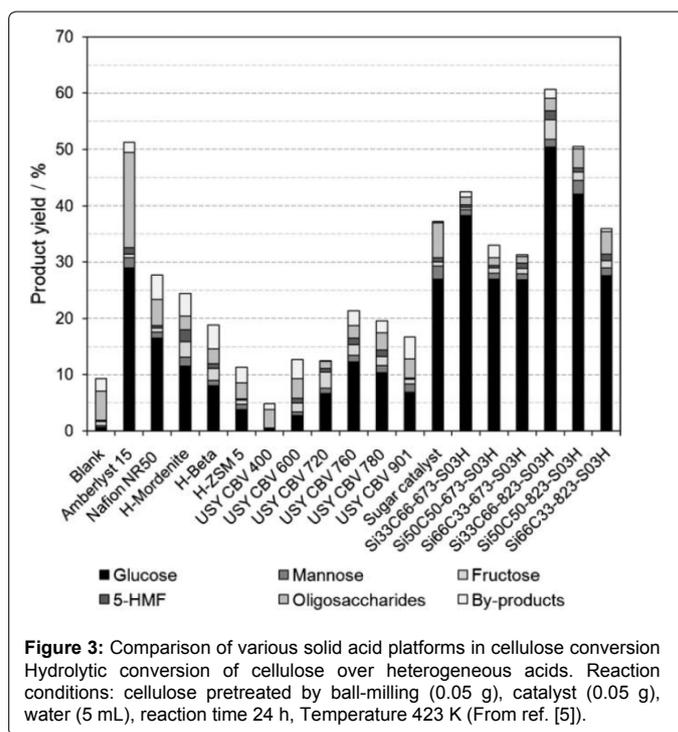


Figure 3: Comparison of various solid acid platforms in cellulose conversion Hydrolytic conversion of cellulose over heterogeneous acids. Reaction conditions: cellulose pretreated by ball-milling (0.05 g), catalyst (0.05 g), water (5 mL), reaction time 24 h, Temperature 423 K (From ref. [5]).

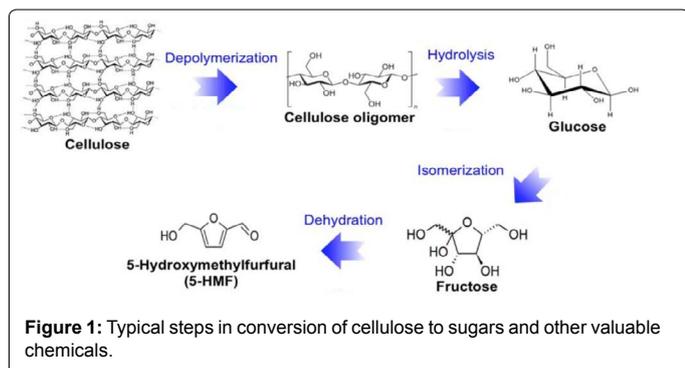
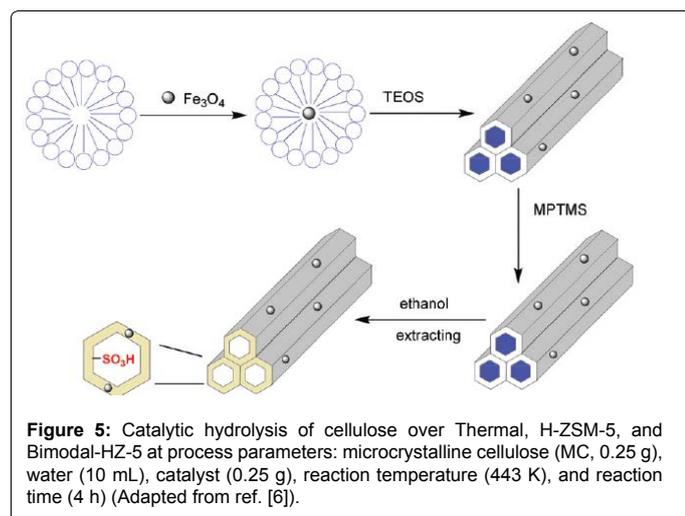
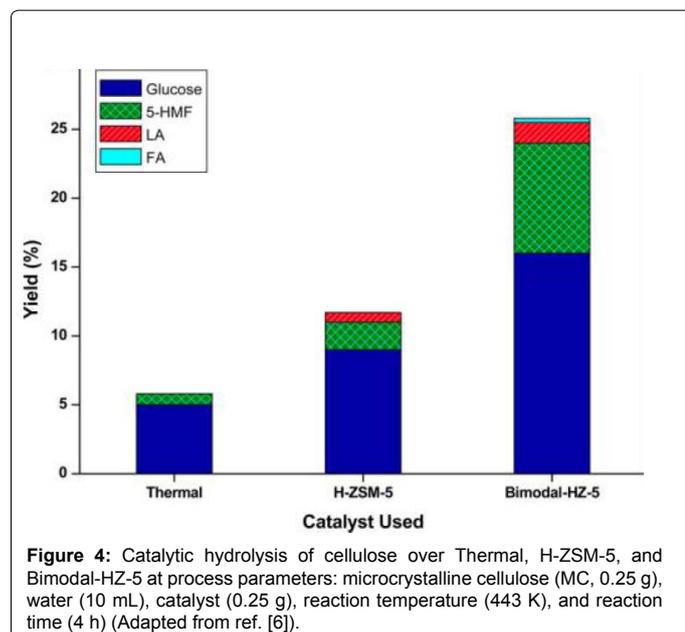


Figure 1: Typical steps in conversion of cellulose to sugars and other valuable chemicals.

acid sites. Further hydrolysis of amorphous cellulose (pretreated with 1-butyl-3-methylimidazolium chloride) with Fe₃O₄-SBA-SO₃H gave a 50% yield of glucose [9].

Conclusions

Mesoporous silica and mesoporous carbon are superb platforms for fabrication of acid catalysts for cellulose hydrolysis provided their large surface area, controlled porosity and the ability to preserve the catalytic group, which translates in high recyclability and high turnover. In addition, the versatility of these materials open a plethora of possibilities toward enhancement of the hybrid catalytic platforms with supplemental capabilities such as magnetic or co-catalytic features.



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