



Structurally tuning microwave absorption of core/shell structured CNT/polyaniline catalysts for energy efficient saccharide-HMF conversion



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ABSTRACT

Microwave absorption and catalytic activity have been synergistically integrated into a core/shell structured CNT/polyaniline (PANI) hybrid catalyst that enables localized heating on the catalyst surface and uplifts energy efficiency in the dehydration reaction of saccharides to 5-hydroxymethylfurfural (HMF). Results reveal that the integration of CNT and polyaniline significantly improves the overall saccharide conversion and HMF yield. The PANI shell thickness and morphology are controlled by both reactant feeding ratio and polymerization reaction rate. A thinner and rougher PANI shell is favourable to enhance the overall microwave absorption, improve heat transfer efficiency to catalyst surface and thus reaction efficiency. The highest energy efficiency of $7.6 \text{ mmol kJ}^{-1} \text{ L}^{-1}$ is reached in 10 min with CNT/PANI catalyst (30 wt% CNTs) and 19 W input power. Moreover, the packing of polyaniline shell on CNT core facilitates its separation from reaction mixture and effectively prevents catalyst loss. These catalysts show excellent recyclability that the catalyst activity can be completely recovered by a simple re-doping process in 1.0 M sulfuric acid. This work opens up a new window in microwave responsive catalyst design that enhances energy efficiency in saccharide-HMF conversion reactions and promotes the economic feasibility of such reactions in practice.

1. Introduction

Exploration of sustainable energy is becoming one of the most pursuing research areas in this century facing the challenge of fossil fuel depletion [1]. The sustainable nature of biomass resources attracts great interests in catalysis, energy storage, environmental remediation, and especially in the synthesis of valuable platform chemicals [2–7]. Among them, synthesis of 5-hydroxymethylfurfural (HMF) from carbohydrate (e.g. cellulose, saccharide) is the most studied reaction and it is considered as an important step in biomass utilization that leads to a variety of valuable chemicals [8,9]. For example, HMF can be rehydrated to levulinic acid or oxidized to furandicarboxylic acid [10,11]. Until now, different catalysts, such as Nb_2O_5 [12], $\text{SO}_4^{2-}/\text{ZrO}_2$ [13], and $\text{VOPO}_4\text{-SiO}_2$ [14] have been developed to maximize the HMF yield by using saccharide as reactant [15]. However, a few major disadvantages of existing reaction systems, such as low HMF yield in aqueous medium, long reaction time, high energy consumption and potential environmental issues by using organic solvent, restrict their further development into practical stage. For instance, using aprotic organic solvent in the reaction can boost HMF yield and suppress side-

reactions, but it comes with a separation process that often consumes a great amount of energy not even mention the potential environmental pollutions. For the selection of catalyst, heterogeneous catalysts could be more advantageous than homogeneous catalysts in terms of easy separation and low risk of corrosion to equipment. However, previous studies revealed that heterogeneous catalysts are easy to lose their activity and the subsequent separation and reactivation processes are often complicated [16].

Conventional dehydration reaction of saccharides often requires long reaction time of several hours or even longer at high temperature. To expedite reaction rate and improve energy efficiency, microwave heating has been used in such reactions [17,18]. In theory, microwave irradiation is able to generate hot-spots in the reaction medium and provide localized heating to accelerate the reaction [19,20]. For example, Carrasquillo-Flores et al. achieved 91% yield of glucose and 96% yield of xylose in the depolymerization reaction of cellulose by using microwave, which is about 6 times the yield compared to conventional heating method at the same reaction condition [21]. Qi et al. found that not only the fructose conversion was improved by using microwave, the 5-HMF yield is also increased in the presence of a cation exchange resin

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catalyst [22]. Realizing the fact that most of existing heterogeneous catalysts (e.g. TiO_2 , Niobic acid and Amberlyst-15) are microwave-transparent [23]. The catalyst itself does not absorb microwave and it does not contribute to the heating of the reaction system. The heat generated from the reaction is mainly contributed by polar solvent such as water. However, all heterogeneous reactions occur at the surface of the catalyst. Localized heat generation from catalyst could be more advantageous in terms of the heat utilization during reaction. Until now, the coupling of microwave irradiation and catalyst design has rarely been investigated.

In a heterogeneous catalytic reaction, microwave energy could be absorbed by both solid catalyst and liquid media by careful material design in the reaction system. The heat generation efficiency depends on many factors including but not limit to the dielectric/electric properties (e.g. complex permittivity and complex permeability) and interface structure of the solid catalyst [24,25]. To expedite the reaction at catalyst surface, it is preferred to allocate more microwave energy to the surface of solid catalyst where reaction occurs. Carbon materials, such as carbon nanotubes (CNTs) [26,27], carbon black [28], graphene [29], and carbon fibers (CFs) [30], are ideal microwave absorbers due to their excellent dielectric polarization properties. However, the inert surface property of carbon materials disqualifies them as suitable catalyst. Even though acidification of carbon materials could be an alternative approach to introduce catalytic function, this process damages the conjugated pi-pi structure of carbon and therefore disables its microwave-absorption property [31,32]. Therefore, integrating carbon material and functional catalyst could be an effective approach to obtain efficient microwave responsive catalyst with sufficient acid sites. Polyaniline (PANI), a well-studied conducting polymer, acquires two major advantages as microwave catalyst. One is the good electrical conductivity and dielectric loss, which ensure excellent microwave absorption property [33]. The other is its abundant acid sites and convenient doping of different acids [34]. For example, Drelinkiewicz et al. used organo-sulfonic acid doped polyaniline as catalyst in transesterification and esterification reactions, where the yield of methyl esters reached up to 90 mol% in 6 h [35].

In this work, microwave responsive core/shell structured hybrid catalysts were successfully synthesized with carbon nanotubes (CNTs) as microwave absorber core and polyaniline (PANI) as catalytically active shell. These catalysts were studied in the microwave-assisted dehydration reaction from saccharides to HMF. The polyaniline shell thickness and structure were controlled to study their effects on microwave absorption as well as catalytic properties. By controlling the input power of microwave irradiation, the microwave absorption capability and catalytic reactivity of such core/shell structured catalysts were evaluated. Finally, the separation and activation of these catalysts were studied in multiple reaction cycles.

2. Experimental

2.1. Materials

CNTs (Pyrograf III PR-24-XT-LHT, $d \approx 50\text{--}100\text{ nm}$, length: $50\text{--}200\text{ }\mu\text{m}$) was obtained from Pyrograf Products Inc. Aniline ($\text{C}_6\text{H}_7\text{N} \geq 99.5\%$), Ammonium persulfate ($\text{APS} \geq 98\%$), D(-)-fructose ($\text{C}_6\text{H}_{12}\text{O}_6 \geq 99\%$), D-(+)-glucose ($\text{C}_6\text{H}_{12}\text{O}_6 \geq 99.5\%$) and sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) were purchased from Sigma-Aldrich. 2,4-pentanedione ($\geq 99\%$) was purchased from Acros Organics. Sulfuric acid (98%) was purchased from Fisher Scientific. Ethanol (200 proof) was purchased from Decon Laboratories, Inc. All reagents were used as received without further purification. Deionized water was purified using a Milli-Q Direct 8 Ultrapure Water system (Millipore, Billerica, MA) with a minimum resistivity of $18.2\text{ M}\Omega\text{ cm}$ and used for all experiments.

2.2. Surface modification of CNTs

CNTs were modified to introduce surface functional groups, e.g. $-\text{OH}$ and $-\text{COOH}$. Briefly, 1.0 g CNTs were added into 50 mL 1.7 M APS and 2.0 M H_2SO_4 mixture solution and ultra-sonicated in a water bath for 3 h. Upon completion, the mixture was kept in an oven at $50\text{ }^\circ\text{C}$ for 17 h. Finally, the functionalized CNTs were rinsed by 100 mL DI water for three times and dried in oven at $60\text{ }^\circ\text{C}$ overnight.

2.3. Synthesis of polyaniline and CNT/PANI catalysts

Core/shell structured CNT/PANI catalysts were synthesized by using a surface-initiated polymerization method [36]. Specifically, certain amount of modified CNTs (0.10, 0.25, 0.43 and 0.66 g representing 10, 20, 30 and 40 wt% of CNTs in the CNT/PANI composites) were initially mixed with aniline/ H_2SO_4 solution (11 mmol aniline in 30 mL 1.0 M H_2SO_4) and then sonicated for 1 h. Then, a mixture of 10 mL 1.3 mmol APS solution and 10 mL 1.0 M H_2SO_4 was added dropwise into the above suspension. Polymerization reaction was carried out at $4\text{ }^\circ\text{C}$ for 20 h. The resulting solids were rinsed with DI water until the filtrate became neutral and then dried at $60\text{ }^\circ\text{C}$. The products were named CP10, CP20 CP30 and CP40 where the numbers represented the weight percentage of CNTs in the CNT/PANI composites. Pure PANI was synthesized following the same procedures without adding CNTs. To control the polymerization reaction, the amount of APS was tuned at 0.4, 1.3, 2.2 and 3.1 mmol while synthesizing CP30 and the products were named as CP30-0, CP30-1, CP30-2 and CP30-3, respectively.

2.4. Characterizations

Catalyst morphology was characterized by scanning electron microscopy (SEM, JEOL-7401, 5 kV) with a sputter-coated silver layer on sample surface. The shell thickness and crystal lattice structure were further characterized by transmission electron microscopy (FEI Scanning TEM) and high resolution TEM (HRTEM, FEI Tecnai G2 F20 ST TEM/STEM & EDAX energy dispersive x-ray spectrometer) at 200 kV. Samples for TEM characterization were prepared by drying a drop of sample powder ethanol suspension on carbon-coated copper TEM grids. The powder X-ray diffraction analysis was carried out with a Bruker AXS D8 Discover diffractometer with GADDS (General Area Detector Diffraction System) operating with a Cu-K α radiation source filtered with a graphite monochromator ($\lambda = 1.541\text{ \AA}$). Brunauer–Emmett–Teller (BET) surface area analysis was measured using a TriStar II 3020 surface analyser (Micromeritics Instrument Corp., USA) by N_2 adsorption–desorption isotherms at 77 K. These samples were pre-treated by N_2 flow at $80\text{ }^\circ\text{C}$ for 12 h. The pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method from the adsorption branch. Elemental analysis of CNT/PANI for C, S and N was performed using a FLASH EA-1112A elemental analyser.

2.5. Catalytic reaction under microwave irradiation

The dehydration reactions were carried out in a microwave tube (10 mL, ID = 12 mm) under microwave irradiation. Typically, 0.55 mmol saccharide and 50 mg CNT/PANI catalyst were added into 4.0 mL water and then sonicated for 5 min. A small stirrer bar was used for mixing during microwave reaction. The loaded tube was then placed into the microwave reactor (Discover SP, CEM) and been exposed to 15 W microwave power for 30 min. After that, the system temperature cooled down to room temperature. The system temperature was measured by infrared technique. The resulting solution was filtered using a syringe filter (VWR, 0.22 mm PTFE). The filtrate was then analyzed by both UV-vis spectrophotometry and HPLC equipped with RI detector and HPX-87 column with 0.17 mL/min of distilled water at $55\text{ }^\circ\text{C}$. The

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