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Facile synthesis of hierarchical porous catalysts for enhanced conversion of fructose to 5-hydroxymethylfurfural

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ABSTRACT

Facile synthesis of solid acid carbonaceous catalysts with hierarchical pore structure has been reported. As carbonaceous catalyst precursor, MOF-derived carbon (MDC) was prepared by a simple heat-treatment of highly crystalline metal-organic framework-5 (MOF-5) without any complicated process and environmental burden. Subsequently, $-SO_3H$ groups with high catalytic activity were successfully grafted onto the carbonaceous support by the sulfonation process. The obtained catalysts, MDC-SO_3H have been systematically studied as acidic heterogeneous catalyst in dehydration of fructose into 5-hydroxymethylfurfural (5-HMF) with isopropanol-mediated DMSO solvent. The experiment results proved that the efficient 5-HMF yield was gained in mixed solvent which a large amount of DMSO was substituted by isopropanol. The highest yield of 5-HMF (89.57%) was obtained at 120 °C for 2 h with the use of 90 vol. % isopropanol as the cosolvent in our experiment. What's more, the catalyst showed excellent recyclability after 5 times catalyze reaction without significant loss of catalytic activity.

1. Introduction

With the threats of energy consumption and environmental deterioration, the sustainable and environmental energy need to be found to solve these problems [1,2]. Biomass, one of the most abundant renewable energy on the earth [3,4], has attracted great research interest to replace the fossil resources for the production of biofuels and valuable chemicals. Among them, the 5-hydroxymethylfurfural (5-HMF) transformed by biomass energy has received more and more attention in recent years because of its wide application in the preparation of medicine, resin fuel and various additives [5,6]. Compared to other feedstock, the 5-HMF from fructose is much more efficient and easier due to the structure of fructose that was more active to dehydration [7]. Therefore, efficient utilization of fructose for the production of chemicals is critical to the biomass transformation in science research and industrial applications [8,9].

Chemical conversions of 5-HMF from fructose via acidic homogeneous/heterogeneous catalysis have been studied widely [10-12]. Acidic homogeneous/heterogeneous catalyst, a crucial factor which influenced reaction rates, product yields and selectivity, has played an important role in the reaction system [13]. Although the acidic homogeneous catalysis has excellent catalytic performance, it is rarely used in recent years because of the disadvantages such as equipment corrosion, environment pollution and separation difficulty [14]. To address this issue, the acidic active sites were introduced onto heterogeneous catalytic with adjustable acidity and porous structure which can improve the selectivity of reaction obviously. Moreover, the development and utilization for acidic heterogeneous catalyst become the main direction of research in recent decades due to its superiorities of recyclability and non-pollution [15].

Recent years, a class of periodic network structure of crystalline porous materials—metal-organic frameworks (MOFs) has attracted more and more research interests in adsorption, separation, catalysis and hydrogen storage [16,17]. MOFs is a kind of organic–inorganic hybrid materials composed of inorganic metal center (metal ions or metal clusters) coordinated with organic ligand to form 3D crystalline structures with porosity by self-assembly mutual connection [18-20]. MOF-derived carbon (MDC) is a sort of carbonaceous materials that can be made by simple heat treatment of MOFs without complicated process and environmental pressure [21]. The MDC was applied in catalyst with the increasing attention of carbonaceous acidic heterogeneous catalyst due to its excel-

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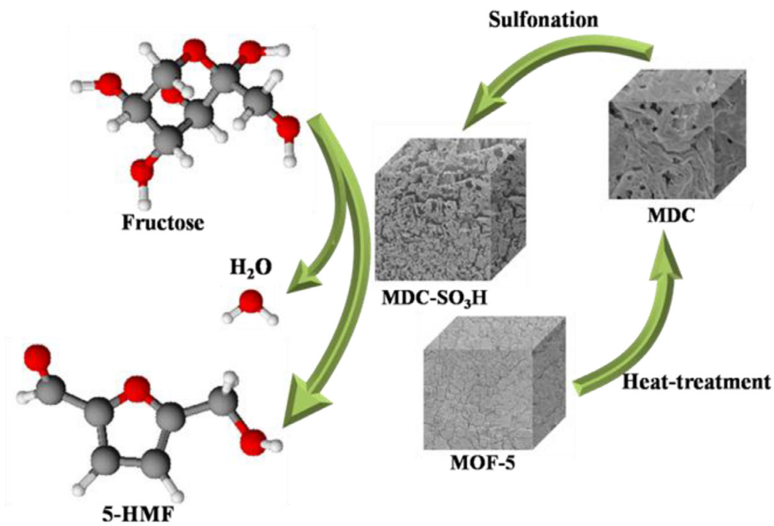

Scheme 1. The synthesis of hierarchical porous catalysts and its catalytic activity for fructose dehydration to 5-HMF.

lent properties including strong thermal stability and hierarchical porous structure. In particular, hierarchical porous structure was essential for the preparation of highly active catalysts due to the following reasons. On the one hand, hierarchical porous structure with a microporous, mesoporous and macroporous structures, was integrated with the characteristics of various pore structures. In addition, it is beneficial to increase the catalytic sites to enhance the catalytic activity of catalyst because of large pore area and developed pore structure [22-24]. On the other hand, hierarchical porous structure was superior to other single structural materials in terms of diffusion and mass transfer, which is beneficial to the contact of the substrate with the active site in the catalyst and facilitate the effective conduct of catalytic reaction [25,26]. In a word, the favorable advantages of the highly porous carbon with high surface areas and excellent thermal and chemical stabilities that is helpful to increase the concentration of acid sulfonic groups on the surface of material [27-29]. What's more, the increasing attention about MOFs as raw material of catalysts on the conversion of fructose into 5-HMF were received in recent years. Hence, it is desirable to take advantage of the MOFs to catalyze dehydration of fructose.

Besides catalysts, green and economical solvent system is another main factor affecting catalytic reaction in fructose dehydration process. At present, a number of different solvent systems were used for carbohydrate dehydration reaction including water, ionic liquids, and aprotic solvent [7]. Water [30-32] is the most ideal green solvent which can dissolve almost all of the sugars. Unfortunately, it has low efficiency of fructose transformation. What's more, the 5-HMF is easy to turn into levulinic acid, formic acid and other by-products in the water [33]. As a result of numerous peculiarities of almost no vapor pressure, non-volatile, non-polluting, high thermal stability and chemical stability and strong solubility, ionic liquids were applied increasingly in chemical processes in recent years [34-36]. Although so many advantages the ionic liquids have, there are some limitations including high cost and difficulty of separation that restrict the application in industrial production. As typical aprotic organic solvents, dimethylsulfoxide (DMSO) shows excellent performance for 5-HMF production from fructose. However, DMSO is not the most ideal solvent because of its high boiling point resulting in that the products separate with difficultly from solvent. In order to alleviate the limitations of DMSO mentioned above, one of the possible solutions was the utilization of green and cost-efficient cosolvent to replace a reasonable amount of DMSO [7]. Wang's group obtained 5-HMF that the yield as high as 87% while using 9:1(v/v) isopropanol/DMSO solvent mixtures as a reaction medium for the dehydration of fructose to 5-HMF [7]. The solvent system mentioned above is more advised to promote the development of the system due to its low-cost, non-pollution and efficiency.

Enlightened by the information mentioned above, poriferous cubic MOF-5 crystal composed of terephthalic acid bridging ligands and $[Zn_4O]^{6+}$ metal cluster center, was chosen for the preparation of carbonaceous catalyst. In this work, the MOF-5 was prepared as the precursor of the carbonaceous catalyst first. Then, the hierarchical pore carbonaceous acidic heterogeneous catalyst named MDC-SO_3H was obtained through heat-treatment and sulfonation. Subsequently, the reaction of fructose to 5-HMF was carried out in solvent system which was mentioned above with MDC-SO_3H under different time, temperature and dosage of catalyst. The technological process of this work was shown in Scheme 1. In addition, the morphology and various properties of catalysts were characterized, and the catalytic performance in fructose into 5-HMF was discussed in detail.

2. Experimental section

2.1. Chemicals and reagents

Fructose (99%), zinc nitrate hexahydrate (AR, 99%), terephthalic acid (BDC, 99%), sodium chloride (AR, 99.5%), sodium hydroxide (AR, 96%) and phenolphthalein (pH indicator) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). N,N' -dimethylformamide (DMF, AR), methylene dichloride (AR), sulfuric acid (98%), dimethysulfoxide (DMSO, AR) and isopropanol (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized water (DI, 18.2 ML cm-1) was obtained through a Milli-Q water-purification system.

2.2. Preparation of MOF-5

Zinc nitrate hexahydrate (1.3388 g, 2.25 mmol) and terephthalic acid (0.1894 g, 1.14 mmol) were dissolved in DMF (30 mL) in a Teflon lined autoclave. The mixture was fully dissolved under ultrasound for 30 min. Then a solvothermal treatment was sequentially performed in an oven at 135 °C for 24 h to promote the formation of cubic crystals of MOF-5. The reaction vessel was removed from oven after 24 h and cooled to room temperature. The crystals were washed with DMF for three times, and soaked in methylene dichlo-