



Dehydration of fructose into 5-hydroxymethylfurfural by high stable ordered mesoporous zirconium phosphate



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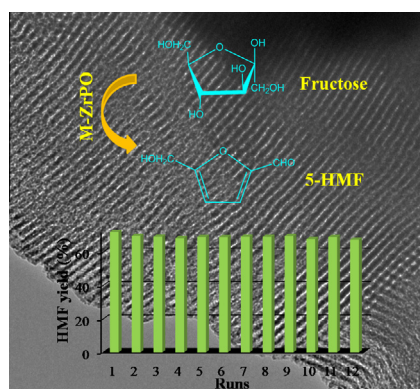
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HIGHLIGHTS

- A series of M-ZrPO have been prepared via evaporation induced self-assembly strategy.
- Superior fructose conversions and 5-HMF selectivity were achieved with M-ZrPO-0.75.
- The M-ZrPO showed excellent structure stability and higher catalytic stability.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, a series of ordered mesoporous zirconium oxophosphate with different P/Zr molar ratios (M-ZrPO-*x*) were prepared via one-pot evaporation induced self-assembly strategy (EISA). The catalytic performance of M-ZrPO-*x* for the dehydration reaction of fructose to produce 5-hydroxymethylfurfural (5-HMF) was also studied. With high concentration of Brønsted and Lewis acid sites measured through NH₃-TPD and pyridine-IR, M-ZrPO-0.75 performed high catalytic activity (up to 97.4%) and selectivity (79.6%) of 5-HMF under relatively mild conditions. Furthermore, M-ZrPO-0.75 performed excellent catalytic stability. Based on detailed analyses of XRD, SEM, TEM, BET and XRF, the structural, surface and textural properties of M-ZrPO-0.75 after reaction were investigated. Obtained results demonstrated that the mesostructure still retained even after twelve cycles, which may be ascribed to the “ordered” mesoporous properties and high thermal stability. In addition, a lower activation energy was obtained in this M-ZrPO catalytic system using dimethyl sulfoxide as solvent.

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1. Introduction

With the increasingly serious environment problem caused by petroleum resources, researchers have given priority to explore renewable resources to replace the fossil fuels avoiding the climate change in future [1]. As a kind of renewable and sustainable fuel,

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biomass resource has recently gained much attention [2,3]. Among numerous biomass-derived chemicals, 5-hydroxymethyl-furfural (5-HMF) is one of the most promising biofuel sources. It has been applied in plastics [4], pharmaceuticals [5] and fine chemicals [6] fields. As a result of the versatile applications of 5-HMF, rapid progress in efficient catalytic systems for the preparation of 5-HMF has been witnessed over recent years.

Several homogeneous catalysts, such as mineral acids [7], metal chlorides [8] and ionic liquids [9] have been employed for the production of 5-HMF with high yield. However, serious drawbacks in terms of equipment corrosion, difficulties in separation and recovery of the catalyst from the reaction mixture [10], limit their further application. Heterogeneous acid catalysts with sustainability and environment friendliness seem more promising for practical applications in agreement with the development of green processes [11]. Up to now, the utilization of heterogeneous catalysts, including ion exchange resins, oxides [12], phosphates [13] and heteropolyacids [14], has been reported.

Recently, porous materials, especially the mesostructured solid acid catalysts, are greatly attractive due to its structural superiorities with large surface areas and large pores [15]. Although quite a few reports are available on the synthesis and catalytic activity of nanopore materials [16], synthesis routes, their properties and applications have been thoroughly studied and have been addressed in comprehensive reviews [17,18]. Among the various types of porous solid acid catalysts, mesoporous zirconium phosphate (ZrPO) materials with high water tolerance ability is relatively stable in solvent [19] showing good active in conversion of carbohydrates to 5-HMF owing to its excellent acidity [20]. Many methods were developed to the synthesis of mesoporous zirconium oxophosphate [21]. However, it is difficult to control the stability of the mesostructures during high temperature calcination and even their mesostructures were damaged after removing the surfactant. Therefore, how to improve the stability of the catalyst became an important subject in the respect of the practical application. In our previous work, ordered mesoporous zirconium oxophosphate (M-ZrPO) with high thermally stability up to 800 °C, has been successfully synthesized [22]. Therefore, considering the strong acid property except for the structure stability of M-ZrPO, we hope to employ it to catalyze fructose into 5-HMF and further improve the reaction stability of catalyst.

In this work, well-ordered zirconium oxophosphate with different molar ratios of P/Zr (from 0.25 to 1.25) was synthesized according our previous study and utilized to promote fructose dehydration reaction. The M-ZrPO exhibited high catalytic activity and catalytic stability in the reaction of conversion of carbohydrates into 5-HMF, which can be ascribed to its unique stability and strong acidic properties. Meanwhile, the regenerated catalyst was characterized to assess its structure stability through detailed measurements of chemical and physical properties. In addition, the activation energy of fructose dehydration reaction catalyzed by M-ZrPO was investigated.

2. Materials and methods

2.1. Materials

(EO)₁₀₆(PO)₇₀(EO)₁₀₆ tri-block copolymer (Pluronic F127) was purchased from Sigma–Aldrich. 5-hydroxymethyl-furfural (98%) and levulinic acids (99%) used as standard analysis agents were purchased from aladdin. All other chemicals were of analytical grade and used without purification.

2.2. Synthesis of catalysts

Ordered mesoporous zirconium oxophosphate materials with different P/Zr molar ratios were prepared through a slow evapora-

tion method using the template agent F127 according our previous work [22] and were denoted as M-ZrPO-x. In a typical procedure, the structure directing agent (F127) (1.2 g) was dissolved completely in anhydrous ethanol (15 ml). Then, ZrOCl₂·8H₂O (5 mmol) and PO(OCH₃)₃ (3.75 mmol), at the molar ratio of P/Zr = 0.75, as the precursors were added into the above solution in the same time and the mixture was stirred for over 6 h, the transparent solution was held at 60 °C for 48 h in order to the volatilization of solvent slowly. Finally, the xerogel was obtained and dried at 100 °C for 24 h. Afterwards, template agent was removed at 500 °C for 5 h and M-ZrPO-0.75 was obtained. Similarly, another four M-ZrPO-x samples (x = 0.25, 0.50, 1.0, 1.25) were synthesized according to the above mentioned procedure.

2.3. Dehydration of fructose

The conversion of fructose was performed in a 5 ml round bottom flask equipped with a condenser and using a preheated oil-bath under magnetic stirring. The typical procedure was as follows: D-fructose (300.0 mg), DMSO (3.0 ml) and powder M-ZrPO (50.0 mg) were added into the flask. The dehydration was started by heating the mixture to the given temperature. After the reaction was completed (typically 90 min), the flask was immediately quenched in a water bath and subsequently the mixture was centrifuged. The supernatant liquid was diluted with Milli-Q water and 50.0% (v/v) acetonitrile aqueous solution respectively for the analysis of fructose consumption and the yield of product.

2.4. Analysis of fructose and 5-HMF

The consumption of fructose was confirmed by measuring its concentration in the aqueous phase by high performance liquid chromatography (Agilent-1100) system which was equipped with a refractive index detector (RI) using PHENOMENEX REZEX RHM-Monosaccharide H+(8%) (300 mm × 7.8 mm, 5 μm). The 5-HMF were determined in 50% (v/v) acetonitrile aqueous solution using HP1090 equipped with DAD detector and a reversed-phase C18 column (250 mm × 4.6 mm, 5 μm).

Conversion of fructose and the yield of products were calculated according to the following equations:

$$\begin{aligned} \text{The conversion of fructose (mol\%)} \\ &= \frac{\text{the molar of fructose converted}}{\text{the molar of initial fructose}} \\ &\times 100 \end{aligned}$$

$$\begin{aligned} \text{The yield of 5-HMF (mol\%)} &= \frac{\text{the molar of 5-HMF produced}}{\text{the molar of initial fructose}} \\ &\times 100 \end{aligned}$$

$$\begin{aligned} \text{The selectivity of 5-HMF (\%)} &= \frac{\text{the molar of 5-HMF produced}}{\text{the molar of fructose converted}} \\ &\times 100 \end{aligned}$$

5-HMF was extracted with ethyl acetate and determined by gas chromatography–mass spectrometry for qualitative analysis. Qualitative analysis of 5-HMF was performed by using an Agilent 7890A gas chromatography fitted with a HP-5 capillary column connected with Agilent 5975C series mass spectrometry equipped with a Triple-Axis detector.

To obtain the reliable data of the reaction, repeated experiments were carried out under identical reaction conditions. The obtained results including conversion of substrate and yield of products were found to be reproducible in the range of ±5.0% variation. The experimental error in injection was below 2%.

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