



Research article

Efficient production of furfural from xylose and wheat straw by bifunctional chromium phosphate catalyst in biphasic systems

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ABSTRACT

We present here a study of the production of furfural from xylose and wheat straw using the chromium phosphate (CrPO₄) with Lewis and Brønsted acidity as a highly efficient catalyst in the water/tetrahydrofuran (THF) biphasic system. The effects of various reaction parameters including reaction temperature, reaction time, system, and catalyst dosage were explored to evaluate the product yield. Under CrPO₄ catalysis, an excellent furfural yield could reach 88% from the xylose at 160 °C for 60 min. Meanwhile, 67% furfural and 32% 5-hydroxymethylfurfural (HMF) were simultaneously achieved from wheat straw at 180 °C for 90 min. Mechanistic studies suggested that the perfect catalytic activity of CrPO₄ was due to its inherent bifunctional catalysis activity. It was found that the CrPO₄ was easily to be recovered and a great catalytic activity was available after four cycles, which not only contributed to a sustainably reduced energy consumption on catalyst recovery, but also reduced the concerns associated with toxic chromium element.

1. Introduction

Nowadays, the scarcity of fossil energy has become a challenge that cannot be ignored in terms of the increasing demand for petrochemical industry. It is necessary to seek abundant and renewable alternative energy sources [1]. Biomass is the only renewable organic carbon source in nature, having the merits of environmental friendly, abundant and low feedstock cost, that endow it with unique advantages in producing fuels and industrially important chemicals [2]. In recent years, the production of high-value chemicals by catalytic conversion biomass and derivatives to has drawn much attention. Furfural is among the most notable versatile platform molecules due to its ability to be further converted to various fuels and useful chemicals, including furfuryl alcohol [3], cyclopentanone [4], 2-methyltetrahydrofuran [5], levulinic acid [6], maleic acid [7] and γ -valerolactone (GVL) [8].

Traditionally, the production of furfural is mainly proceeded via dehydration of C5 sugar in the aqueous phase over homogeneous catalysts such as H₂SO₄ and HCl [9,10]. However, the yield and selectivity of furfural was poor, not to mention environmental pollution, health risk concerns and corrosion equipment. As a new homogeneous catalyst, ionic liquids have the ability to achieve high yield and selectivity of furfural [11–13]. Unfortunately, the disadvantages of difficult separation and high cost limit the further industrial application of ionic

liquids. To overcome the shortcomings in homogeneous catalysts, a great deal of effort was focused on the development of more efficient, inexpensive and easily separated heterogeneous solid acid catalysts, including resins [14], sulfonated carbon [15], metal oxides [16], mesoporous silica [17], zeolites [18] and heteropolyacids [19]. For example, in the work reported by Kim and co-workers [20], H-ZSM-5 catalyst supplied a yield of around 43% furfural from xylose in the water/toluene biphasic system at 140 °C for 240 min. Similarly, Zhang et al. [15] described a carbon solid acid-catalyzed process of dehydration of xylose to furfural and achieved 78.5% furfural under optimal reaction conditions (170 °C, 30 min). Additionally, Agirrezabal-Telleria et al. [21] used arenesulfonic SBA-15 catalysts to catalyze xylose dehydration, acquiring an outstanding 82% furfural yield in the water/toluene biphasic system at 160 °C. In another study, Zhang et al. [22] investigated the catalytic performance of SO₄²⁻/ZrO₂-TiO₂ catalyst for the conversion of xylose and glucose mixtures to furfural and HMF. Under the optimum conditions, 30.9% HMF and 54.3% furfural were produced in the water/*n*-butanol biphasic system.

Despite the fact that the heterogeneous catalysts described above exhibit good catalytic activity for the catalytic furfural formation, nevertheless, one shortcoming also hinder their large-scale use, that is, complex preparation process. In order to solve this challenge, solid phosphates gained a wide range of concerns in recent years because of

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their low price and simple structure, and their mostly weak electrolytes, which can be used as solid acid catalysts in the preparation of HMF and furfural. Nijhuis and co-workers [23] demonstrated that aluminum, titanium, zirconium, and niobium-based phosphates were capable of providing HMF with a selectivity range of 30%–60% using glucose as feedstock. Maximum yields of HMF of 77% and 50% were achieved from fructose and glucose, respectively, using large-pore mesoporous tin phosphate in a water/methyl isobutyl ketone biphasic solvent [24]. Xia et al. [25] used FePO_4 and NaH_2PO_4 as co-catalyst, obtaining an excellent 92% furfural yield from wheat straw at 150 °C for 60 min. Sun et al. [26] achieved up to 78% furfural selectivity with the mesoporous tantalum phosphate catalyst, and the catalyst retained considerable catalytic activity after three cycles. Niobium phosphate [27] has also been shown to be a useful solid acid catalyst for the conversion of xylose to furfural and achieved a 43% furfural yield at 160 °C for 30 min.

In this work, we developed an inexpensive CrPO_4 catalyst to synthesize furfural from xylose and wheat straw, which had not only excellent catalytic activity similar to ionic liquid catalyst but also exhibited a preferred reusability. To the best of our knowledge, the use of CrPO_4 catalyst in the conversion of biomass into furfural has not been reported yet. It was found that CrPO_4 as a bifunctional catalyst significantly promoted the formation of furfural from xylose and the efficient catalytic performance was also suitable for the conversion of wheat straw. Moreover, the recyclability of CrPO_4 was also investigated, and the results indicated that the desired furfural yield was available after four cycles. More interestingly, after the reaction was complete, the partially dissolved CrPO_4 was precipitated with the cooling of the temperature. Combining this phenomenon, the possible conversion mechanism of biomass into furfural catalyzed by the bifunctional CrPO_4 catalyst was discussed.

2. Methods

2.1. Materials

D-(+)-Xylose, $\text{FePO}_4 \cdot 4\text{H}_2\text{O}$, $\text{Zn}_3(\text{PO}_4)_2$, $\text{Co}_3(\text{PO}_4)_2$, 4-methyl-2-pentanone (MIBK) and 2-methyltetrahydrofuran (MeTHF) were supplied by Aladdin (China). AlPO_4 was purchased from the Sigma-Aldrich (China). $\text{CrPO}_4 \cdot 4\text{H}_2\text{O}$, and InPO_4 were obtained from Alfa Aesar. Zeolite catalyst HZSM-5 was purchased from The Catalyst Plant of Nankai University Catalyst Co., Ltd (Tianjin, China). Hydrochloric acid (HCl, 36–38%), sulfuric acid (H_2SO_4 , 95–98%), $\text{CrCl}_3 \cdot 4\text{H}_2\text{O}$, tetrahydrofuran (THF), toluene, *n*-butanol, 2-butanol and sodium chloride (NaCl) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Wheat straw was collected from Hebei province, China. The wheat straw raw material was ground until the whole sample passed through a 40-mesh screen, and then washed with deionized water to remove dust on the material. After that, the prepared wheat straw particles were dried in an oven at 80 °C for 48 h. The composition of wheat straw was determined by the standard NREL laboratory analytical procedures [28], the content is as follows: ash (9.8%), glucan (35.5%), xylan (21.9%), arabinan (2.1%), galactan (1.6%), lignin (20.1%) and others (9%).

2.2. Catalyst characterization

FTIR spectra of fresh $\text{CrPO}_4 \cdot 4\text{H}_2\text{O}$ and the precipitated catalyst were recorded on a Thermo Nicolet Nexus 470 spectrometer in the range from 400 to 4000 cm^{-1} . The Cr content of the water solution after the reaction was measured by atomic absorption spectroscopy (AAS). XRD patterns were recorded on a Rigaku Ultima IV X-ray diffractometer equipped with a $\text{Cu K}\alpha$ X-ray source operating at 40 kV and 30 mA. The scanning range (2θ) was from 5 to 80°, with a scanning rate of 20° min^{-1} and a step function of 0.02. GC–MS was used to analyze the liquid products produced from the catalytic conversion of reactants. The products were analyzed by a GC chromatography (Agilent

Technologies 7890A) equipped with a capillary column (Agilent PH-5; 0.32 mm \times 30 m) and flame ionization detector (FID) under ramping temperature from 40 to 280 °C. Mass spectrometric analysis of the liquid products was performed with a 5975C inert MSD mass analyzer (Agilent Technologies) employing Triple-Axis Detector.

2.3. Catalytic activity testing

The conversion of xylose and wheat straw into furfural was carried out in a 100 mL high-pressure autoclave with mechanical stirrer at the desired temperature with stirring speed of 500 rpm. In a typical run, a mixture of xylose or wheat straw (1.0 g), catalyst (0.15 g) and solvent (30 mL THF and 10 mL H_2O saturated with NaCl) was loaded into the autoclave and sealed. The time for the reactor to heat from the ambient temperature to the desired temperature was set to 50 min. Once the reaction temperature was reached, the monitoring of the reaction started. After the reaction was terminated, the condensed water was used to rapidly reduce the temperature of the reactor. Subsequently, the liquid products were collected by filtration, diluted with deionized water, and the filtrate analyzed using HPLC.

2.4. Analysis of products

The concentration of furfural in the aqueous and organic phases was determined by using HPLC (Shimadzu LC-2010AHT) with an XDB-C18 column and a UV detector at 280 nm. The mobile phase was a solution of water and methanol (3/7, v/v) at a flow rate of 0.5 mL/min and the temperature of the column oven was maintained at 35 °C. Since the xylose content in the organic phase was negligible, the xylose concentration refers to the concentration in the aqueous phase. The xylose concentration in the aqueous phase was analyzed by using HPLC (Agilent 1200) equipped with a column (Agilent Hi-Plex H) and a Refractive Index detector. The column temperature was kept at 60 °C and the mobile phase was DI water at a flow rate of 0.5 mL/min. The xylose conversion, furfural yield, and HMF yield are defined as follows:

$$\text{xylose conversion (mol\%)} = \frac{\text{moles of xylose reacting}}{\text{moles of xylose starting}} \times 100$$

$$\text{furfural yield from xylose (mol\%)} = \frac{\text{moles of furfural produced}}{\text{moles of xylose put into the reactor}} \times 100$$

$$\begin{aligned} \text{furfural yield from wheat straw (mol\%)} \\ = \frac{\text{moles of furfural produced}}{\text{moles of xylose units in wheat straw}} \times 100 \end{aligned}$$

$$\begin{aligned} \text{HMF yield from wheat straw (mol\%)} \\ = \frac{\text{moles of HMF produced}}{\text{moles of glucose units in wheat straw}} \times 100 \end{aligned}$$

3. Results and discussion

3.1. Effect of reaction temperature and time on the conversion of xylose into furfural

The effect of reaction temperature on the production of furfural from xylose in the H_2O /THF biphasic system using CrPO_4 as catalyst was first examined in a temperature range from 140 °C to 180 °C and the corresponding results are summarized in Fig. 1. It can be clearly observed that the temperature played a crucial role in the formation of furfural from xylose. A lower furfural yield of 47% with a xylose conversion of 72% was provided when the reaction was conducted at 140 °C. With a further increase in temperature, the furfural yield and xylose conversion were increased sharply, and a considerable 66% furfural yield was obtained as the temperature reached 150 °C. Notably,

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