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Effect of calcination temperature on catalytic performance of alkaline earth phosphates in hydrolysis/dehydration of glucose and cellulose

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HIGHLIGHTS

- The effect of calcination temperature of alkaline earth phosphate catalysts.
- The hydrolysis/dehydration of glucose and cellulose to 5-hydroxymethylfurfural.
- The calcination temperature greatly influenced the crystalline phases and activity.
- The incorporation of Ca and Sr into phosphate can improve the catalytic performance.
- The α-$Sr(PO_3)_2$ (calcined at 900 °C) showed the best catalytic activity.

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ABSTRACT

The hydrolysis/dehydration of glucose and cellulose to 5-hydroxymethylfurfural (HMF) catalyzed by alkaline earth phosphates was investigated under hot compressed water condition. The catalysts were synthesized by reactions of $CaCO_3$ or $SrCO_3$ with ortho-H_3PO_4 via conventional precipitation method in acetone–water media system. The experimental results revealed that the calcination temperature greatly influenced the crystalline phases of the catalysts and the catalytic activity. The calcium and strontium phosphate catalysts without calcination are $Ca(H_2PO_4)\cdot H_2O$ and $Sr(H_2PO_4)_2$, respectively. The calcium phosphate catalysts calcined at 600 and 900 °C are β-CaP_2O_6 while the strontium phosphate catalysts display $Sr_2(PO_3)_4$, and α-$Sr(PO_3)_2$, respectively. The incorporation of Ca and Sr into phosphate network of calcined samples can further improve catalytic performance. Among all synthesized catalysts, the α-$Sr(PO_3)_2$ calcined at 900 °C showed the best catalytic activity, providing the HMF yield of 21.0% from glucose dehydration and total yield of glucose and HMF of 34.8% from hydrolysis coupling dehydration of cellulose.

1. Introduction

Acid catalyzed hydrolysis/dehydration of cellulose feedstocks to furan compounds has drawn increasing attention for years because furan serves as a key player bridging between biomass chemistry and biorefining industry [1,2]. Among various furan compounds, 5-hydroxymethylfurfural (HMF) has been considered a promising platform for producing fine chemicals, pharmaceuticals, and polymers [3].

Many types of acid catalysts have been used in this reaction process, such as, mineral acids [4–6], organic acids [5], H-zeolite [7], ion-exchange resins [8], and sulfonic-acid-modified silica [9]. Generally, the dehydration of sugars (glucose, fructose, and xylose) can be catalyzed by mineral acids such as H_2SO_4, HCl, H_3PO_4, and HNO_3 [3]. For instance, Asghari and Yoshida [6] studied the decomposition of fructose using mineral acids (HCl, H_2SO_4, H_3PO_4) and organic acids (citric acid, maleic acid, p-toluenesulfonic acid (PTSA), oxalic acid) in comparison with non-catalytic system under sub-critical water. The results showed that the conversion of fructose to HMF increased in the presence of acids. H_3PO_4 has been reported to give a good balance between activity and product yield. For instance, Ray et al. [10] indicated that 0.01 mmol H_3PO_4 can form 10.8% of HMF from fructose dehydration at 80 °C in 1-butyl-3-methylimidazolium chloride [BMIM]Cl. In addition, the decomposition of real biomass, e.g., Japanese red pine wood, was investigated under H_3PO_4 condition [11]. It was found that H_3PO_4 showed the ability for the hydrolysis and dehydration of biomass

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to produce water-soluble saccharides and HMF, respectively. To make the catalytic system more eco-friendly, reusable and less corrosive heterogeneous catalysts have been developed for the biomass conversion.

Metal phosphates are the phosphates in a form of solid catalysts, and well known for their acid properties. Asghari and Yoshida [12] studied the dehydration of fructose to HMF using zirconium phosphate as solid catalysts under sub-critical water condition. They found that zirconium phosphates were stable under sub-critical water condition, and were easily recovered and regenerated. Moreover, Gu et al. [13] investigated metal phosphates of tin, zirconium, and titanium for dehydration of sorbitol to isosorbide. They discovered that the acidity caused by functional groups of the catalysts was the direct factor for catalyst lifetime. Tin phosphate showed the highest selectivity and lowest deactivation rate. Bautista et al. [14] studied phosphates of Al, Fe, Ni, and Mn on cyclohexanol dehydration. They found that the presence of Al in mixed $FeAl(PO_4)_2$ and $Ca_3Al_3(PO_4)_5$ showed the highest catalytic activity. Carlini et al. [15] used vanadyl phosphate-based catalysts, containing different trivalent metals (Fe^{3+}, Cr^{3+}, Ga^{3+}, Mn^{3+}, and Al^{3+}), as acid catalysts in the dehydration of fructose to HMF. Fe-substituted vanadyl phosphate afforded the best catalytic system in terms of both activity and selectivity.

In our previous work, we found that the catalytic activity of the phosphate catalyst, i.e., copper, strongly depended on the heat treatment process or calcination temperature [16]. The results showed that the phosphates of copper calcined at 900 °C synthesized by precipitation process in the acetone–water media system exhibited superior catalytic activity and HMF yield to as-synthesized and calcined samples at 600 °C. Therefore, in this context, we have reported the use of simple metal phosphates i.e., Ca and Sr phosphates due to their cost effectiveness and potential function. The role of phosphate structure, crystalline phase, and acidity upon calcination at various temperatures were studied in biomass and sugar conversion which is an important reaction in biorefinery application.

2. Experimental

2.1. Catalyst synthesis

The alkaline earth phosphates of strontium and calcium were synthesized using conventional precipitation in the acetone–water media system. Calcium carbonate ($CaCO_3$), strontium carbonate ($SrCO_3$) and ortho-phosphoric acid (o-H_3PO_4) were selected as Ca, Sr, and P precursors, respectively. A 0.1-g quantity of $CaCO_3$ or $SrCO_3$ was dissolved in 5 cm^3 of 70% ortho-H_3PO_4 aqueous solution. Next, a 30-cm^3 amount of acetone was added to the solution being vigorously stirred for 1 h. The precipitated products were filtered and washed with acetone several times. After that, the obtained samples were dried in an oven overnight, and then were calcined in air at 600 and 900 °C for 3 h.

2.2. Characterization techniques

The specific surface areas of all catalysts were determined by conventional N_2 sorption at 77 K (BELSORP-max, BEL, Japan). The crystalline structures of the catalysts were analyzed by X-ray diffraction (XRD, Bruker D8 Advance, Germany) using a Cu K_α radiation at 40 kV and 40 mA with a scanning rate of 0.02°/min from 2θ = 10–60. Morphology of the catalysts was observed by scanning electron microscopy (SEM, S-3400, Hitachi, Japan). Moreover, acid strengths were examined via several indicators including neutral red (pK_a = +6.8), methyl red (pK_a = +4.8), dimethyl yellow (pK_a = +3.3), crystal violet (pK_a = +0.8), 4-(phenylazo)diphenylamine (pK_a = +0.42), and dicinnamalacetone (pK_a = −0.3).

2.3. Catalytic test

The experimental apparatus consists of a stainless steel tube reactor (1.27 cm O.D. and 10 cm length), a furnace heater, and a temperature controller. The reactor was mounted vertically inside a furnace equipped with a rotor to shake vertically to enhance the mixing state. The temperature was monitored using a K-type thermocouple inserted into the middle of the reactor.

The reactions were carried out in a batch-type reactor with an inner volume of 10 cm^3. A mixture of glucose or cellulose (0.1 g), distilled water (1 cm^3), and solid catalyst (0.01 g) was added into the reactor. Nitrogen was then loaded to raise the reactor pressure to 2.5 MPa. H_3PO_4 was used as a reference homogeneous catalyst, and the reaction tests were done at 0.1 M concentration of H_3PO_4. Next, the reactor was heated to 220 °C for dehydration of glucose and 230 °C for hydrolysis/dehydration of cellulose. The reaction time was counted after the inside temperature of reaction tube reached the desired temperature. The reactor vessel was immediately immersed into tap water to stop the reaction. The experiments were done in triplicate to get more accurate results; the obtained results were shown as average values ± standard deviations. The amount of product species in liquid samples was quantitatively analyzed by an HPLC with a Shodex RSpak KC811 column coupled with UV detector for furan compounds, and with a Shodex Sugar SP810 column coupled with reflective index (RI) detector for sugars. The amount of metal leaching in the reaction media after the reaction tests was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES, JOBIN YVON HORIBA, ULTIMA 2 C).

The equations for calculation of conversion of glucose, HMF yield and glucose yield were shown in Eqs. (1)–(3), respectively. Eqs. (1) and (2) are used for the case of glucose feedstock. In the case of cellulose feedstock, yields of major products, i.e., HMF and glucose are calculated by Eqs. (2) and (3), respectively:

$$\text{Conversion of glucose } (\%) = 100\left(\frac{\text{gram of glucose feedstock} - \text{gram of glucose in product}}{\text{gram of glucose feedstock}}\right) \quad (1)$$

$$\text{HMF yield } (\%) = 100\left(\frac{\text{gram of HMF in product}}{\text{gram of glucose or cellulose feedstock}}\right) \quad (2)$$

$$\text{Glucose yield } (\%) = 100\left(\frac{\text{gram of glucose in product}}{\text{gram of cellulose feedstock}}\right) \quad (3)$$

3. Results and discussion

3.1. Properties of the phosphate catalysts

The BET surface area of all alkaline earth phosphate catalysts was about 0.5 $m^2\ g^{-1}$, suggesting their less-porous structures. The XRD patterns of the Ca and Sr phosphate catalysts are presented in Figs. 1 and 2, respectively. Generally, alkaline earth phosphates could be synthesized by several methods, including hydrothermal synthesis [17], microwave assisted method [18], precipitation [19], and sol gel method [20]. The method used in each case depends on the desired type of morphology, structure, and chemical composition. An important step for synthesis of alkaline earth phosphates was suggested to be an acid-heat treatment of raw materials [21]. In this work, alkaline earth phosphate samples were prepared by conventional precipitation method using $CaCO_3$ or $SrCO_3$ with ortho-H_3PO_4 in acetone–water media. From the XRD