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Note

Conversion of fructose, glucose, and cellulose to 5-hydroxymethylfurfural by alkaline earth phosphate catalysts in hot compressed water

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ABSTRACT

The phosphates of alkaline earth metals (calcium and strontium) synthesized by precipitation process in acetone–water media system were used as catalysts for converting fructose, glucose, and cellulose to 5-hydroxymethylfurfural (HMF) under hot compressed water condition. It was found that the phosphates of calcium and strontium effectively catalyzed the HMF formation from fructose and glucose dehydration and cellulose hydrolysis/dehydration reaction, as compared with the non-catalytic system. The XRD analysis confirmed the CaP_2O_6 and α-$Sr(PO_3)_2$ crystalline phases of the catalyst samples, while acid strength of both catalysts was in a range of $+3.3 \leqslant H_0 \leqslant +4.8$. From the study, CaP_2O_6 and α-$Sr(PO_3)_2$ showed similar catalytic performance toward the dehydration of sugars, providing the HMF yields of 20–21% and 34–39% from glucose and fructose, respectively; whereas the total yield of glucose and HMF from the hydrolysis/dehydration of cellulose over α-$Sr(PO_3)_2$ (34%) was higher than that over CaP_2O_6 (17.4%).

Petroleum is not only a major resource for production of liquid fuels for transportation but also a basis for production of chemicals and polymers in various industries.[1] However, petroleum is an unsustainable resource, and its utilization has strong impacts on the global environment. These limitations of petroleum have driven research on the development of renewable energy. Biomass could be utilized as renewable fuel and chemicals via catalytic conversion processes.[2,3]

Aqueous-phase processing of biomass could be performed under moderate to high pressure and temperature, which is generally known as hydrothermal or hot compressed water (HCW) conditions. It is necessary to develop methods for controlling functionality of biomass in targeted products by using various types of reactions, catalysts, and reaction condition to produce desired chemicals.[4–7] The catalysts used in HCW could be either homogeneous or heterogeneous catalysts. Heterogeneous or solid catalysts have several advantages over homogeneous ones such as lower environmental impacts and reusability. However, the catalytic performance of the solid catalysts still needs improvement to overcome the solid catalyst system. Metal phosphates are well known for their acid properties. Asghari et al.[8] studied the dehydration of fructose to HMF by using zirconium phosphates as catalysts under subcritical water condition. They discovered that zirconium phosphates were stable under subcritical water condition and can easily be recovered, regenerated, and used for several runs. Moreover, Gu et al.[9] used metal (IV) phosphates of tin, zirconium, and titanium for dehydration of sorbitol to isosorbide. Tin phosphate showed the highest selectivity and lowest deactivation rate. Moreover, Bautista et al.[10] investigated a series of phosphates (Al, Fe, Ni, and Mn) on cyclohexanol dehydration, and found that the presence of aluminium in mixed $FeAl(PO_4)_2$ and $Ca_3Al_3(PO_4)_5$ showed the highest catalytic activity in conversion of cyclohexanol. Likewise, Carlini et al.[11] 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. To the best of our knowledge, the dehydration of sugars and cellulose to HMF catalyzed by alkaline earth phosphates has not been reported, however.

In the present work, alkaline earth phosphates including Ca and Sr were synthesized via modified co-precipitation method, and proposed as catalysts for the conversion of fructose, glucose, and cellulose to HMF in hot compressed water. The catalyst property and the catalytic performance of the phosphate catalysts were investigated and discussed in comparison with the noncatalytic and homogeneous catalytic systems based on the experimental results.

The BET surface area of all prepared phosphate catalysts was ca. 0.5 $m^2\ g^{-1}$, suggesting the nonporous structures. The XRD patterns of the catalysts are presented in Figure 1. All detectable peaks of

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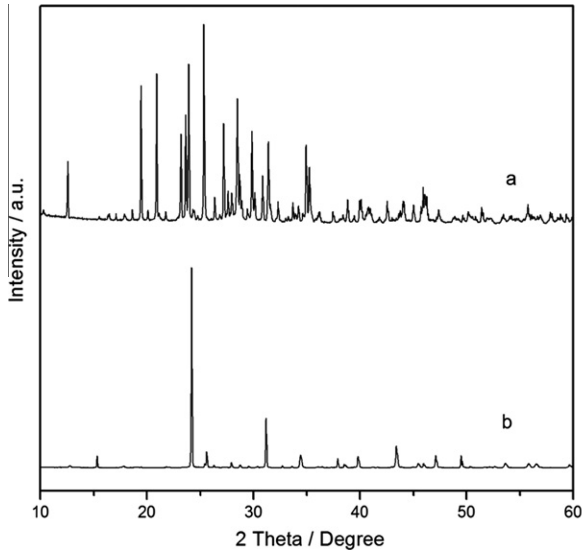

Figure 1. X-ray diffraction patterns of (a) CaP_2O_6 and (b) α-$Sr(PO_3)_2$.

the calcium and strontium phosphates are indexed as CaP_2O_6 (calcium phosphate) and α-$Sr(PO_3)_2$ (α- strontium polyphosphate), which are identified in reference to the standard data of PDF no. 00-011-0039 and PDF no. 00-012-0366, respectively. The single phase of the phosphate with well-crystallized structures was obtained after the high temperature calcination at 900 °C. As shown in Figure 2, the SEM images of the calcium phosphate suggest that the samples are in the form of sintered materials of primary particles whose size were in the range of 100–500 nm. The grain boundary of primary particles in α-$Sr(PO_3)_2$ sample could not clearly be observed, and its sintered form was in an irregular shape. From microscopic view, the surface roughness of the α-$Sr(PO_3)_2$ was clearly less than that of the Ca one. These dense forms of sintered materials were consistent with the results of N_2 sorption analysis, suggesting no internal pore and low specific surface area of the samples. According to the acid property measurement, the CaP_2O_6 and α-$Sr(PO_3)_2$ catalysts have acid strength in the same range of $+3.3 \leqslant H_0 \leqslant +4.8$, whereas the acid strength of phosphoric acid was in a range +0.8 to +3.3. Lower values of H_0 correspond to greater acid strength. The results suggested that all catalysts showed weak acid strength.

The dehydration of fructose and glucose was studied under HCW conditions at 200 and 220 °C for 5 min. The experiments were done with and without the catalyst in order to demonstrate the existence of catalytic activity of prepared solid catalysts under HCW. Figure 3 shows the conversion and HMF yields of fructose and glucose dehydration. Generally, the dehydration of sugars (fructose, glucose, and xylose) can be catalyzed by protonic acids such as H_2SO_4, H_3PO_4, and HCl.[12] It was previously reported that H_3PO_4 provided high activity for dehydration of sugars,[13–15] and was tested for activity comparison in this context. Similar to our experiments,[12,15] Ray et al., for instance,[16] reported that 0.1 mmol H_3PO_4 can form 10.8% of HMF from fructose dehydration at 80 °C in 1-butyl-3-methylimidazolium chloride [BMIM]Cl. Therefore, in this study synthesized phosphate catalysts were investigated in comparison with phosphoric acid.

As shown in Figure 3, the fructose conversion was nearly comparable at 83–93% with or without catalysts at 200 °C. The HMF yield of fructose dehydration was obtained at 28.2%, 34.1%, and 39.3% over H_3PO_4, CaP_2O_6, and α-$Sr(PO_3)_2$, respectively. Without catalyst, the HMF yield was relatively low at 21.5%. On the other hand, the improved selectivity to HMF was obtained over the solid catalysts. Moreover, the HMF yield from fructose dehydration increased by ca. 10% when reaction temperature increased from 200 to 210 °C. Under the same amount of phosphoric acid catalyst (10^{-4} mol), Ray et al.[16] reported that HMF yield was obtained at 10.8%.

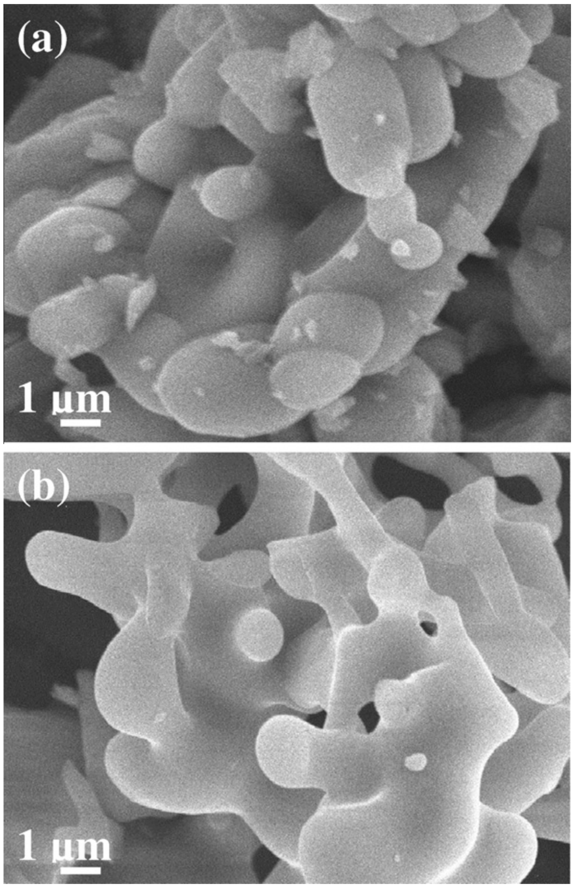

Figure 2. SEM micrographs of (a) CaP_2O_6 and (b) α-$Sr(PO_3)_2$.

The glucose conversion and the HMF yield from glucose in the presence of phosphoric acid and alkaline earth phosphate catalysts was obviously higher than that in the absence of the catalysts. Glucose conversion was elevated by ca. 30% when homo- or heterogeneous catalysts were employed. This result indicated that these catalysts can effectively enhance glucose conversion, especially heterogeneous phosphate catalysts. Among them, α-$Sr(PO_3)_2$ provided the highest HMF yield of 21%. It can be suggested the phosphate catalyst with weak acid strength could properly catalyze the glucose conversion to HMF. The XRD analysis confirmed the stable phase of the phosphate catalysts after the reaction tests. In comparison with the reported catalysts including TiO_2 and ZrO_2, the present phosphate catalysts outperformed the TiO_2 and ZrO_2 catalysts in glucose dehydration.[17] Qi et al.[17] has reported the HMF yields catalyzed by TiO_2 and ZrO_2 at 18.6% and 10.0%, respectively, while the present CaP_2O_6 and α-$Sr(PO_3)_2$ yielded HMF at 20% and 21%, respectively. Of note that HMF yields from those catalysts in fructose dehydration were nearly comparable.

In addition, Figure 3 shows the product yields of glucose and HMF from hydrolysis/dehydration of cellulose implemented at reaction temperature of 230 °C for 5 min in the absence and presence of catalysts. Cellulose transformation is generally performed under hydrothermal condition with homogeneous or heterogeneous catalysts in aqueous phase. Under this condition, crystalline cellulose undergoes transformation to amorphous state followed by dissolution to produce glucose. The primary products of cellulose transformation in this work are glucose and HMF. Without catalyst, hydrolysis coupling dehydration of cellulose produced

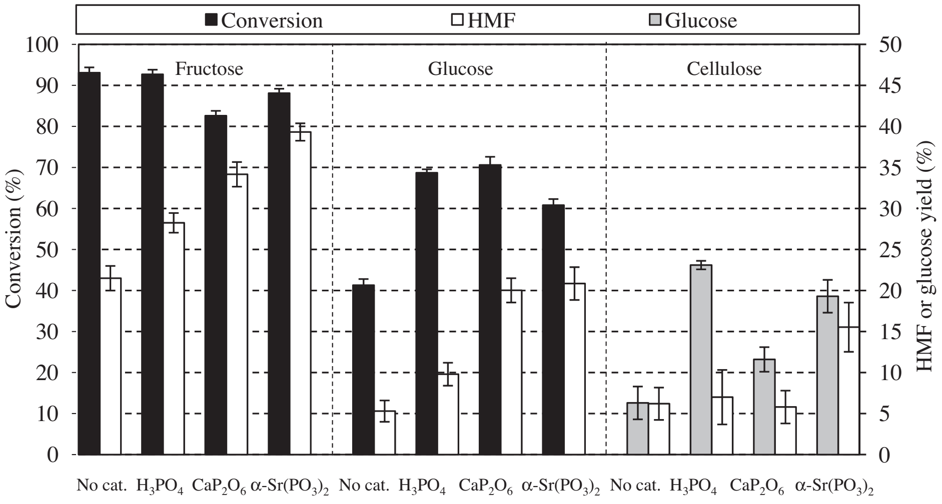

Figure 3. The conversions and product yields of fructose, glucose, and cellulose without catalyst and with H_3PO_4, CaP_2O_6, and α-$Sr(PO_3)_2$. Reaction conditions: temperature = 200 °C (fructose), 220 °C (glucose), 230 °C (cellulose); catalyst loading = 0.1 M H_3PO_4 or 1 wt.% phosphate catalyst.

small quantities of products: glucose (6.3%) and HMF (6.2%). The Ca and Sr phosphates gave comparable yields of glucose at ca. 11.6–19.3%. The yield of HMF over Sr phosphate (15.0%) was higher than that over Ca phosphate (5.8%). It should be noted that furfural could also be produced at relatively low yield of 1–2%, while fructose was not observed in the tests. The total yields (glucose, HMF, and furfural) from cellulose transformation over α-$Sr(PO_3)_2$ were exceptionally high at 35.4%.

The CaP_2O_6 and α-$Sr(PO_3)_2$ phosphate catalysts can promote the HMF formation from glucose and fructose. When cellulose was used as a feedstock, α-$Sr(PO_3)_2$ can produce glucose and HMF with high yields when compared to the no-catalyst system. However, the HMF yield from cellulose conversion catalyzed by CaP_2O_6 at 230 °C was just comparable to the no-catalyst system. It was experimentally observed that the HMF yield from glucose conversion catalyzed by Ca phosphate significantly dropped when the reaction temperature increased from 220 to 230 °C. It was considered that other side-reactions were strongly accelerated over the Ca phosphate at such a high temperature. The detail investigation on the effect of reaction temperature will be shown in the latter part.

It was proposed that the mechanism of biomass conversion to HMF would follow the reaction steps as follows: (1) biomass hydrolysis to glucose, (2) isomerization of glucose to fructose, and (3) fructose dehydration to HMF. According to the results shown in Figure 3, the formation of HMF from fructose was nearly comparable over CaP_2O_6 and α-$Sr(PO_3)_2$. Both Ca- and Sr-catalysts were highly effective in isomerizing glucose to fructose, resulting in the improvement of HMF yield. The isomerization of glucose to fructose is considered a rate determining step in converting glucose to HMF, and would start from the ring-opening of glucose to open-glucose, and then the open form of glucose is tautomerized to 1,2-enediol intermediate which is finally isomerized to open form of fructose by 1,2-hydride shift.[15] Of note that the biomass conversion catalyzed by H_3PO_4 provided a high yield of glucose of 23% since biomass can be easily accessed by H_3PO_4 solution.

As shown in Figure 4, the effect of reaction temperature on the dehydration of glucose in the presence of H_3PO_4, CaP_2O_6, and α-$Sr(PO_3)_2$ was studied under hot compressed water conditions in the temperature range of 200–230 °C. It can be seen that glucose conversion and HMF yield increased with increasing temperature. HMF yield was highest at 220 °C and decreased with increasing temperature to 230 °C for all cases. Particularly, the drastic decrease in HMF yield was observed over CaP_2O_6 at such a high temperature, corresponding to the low activity of CaP_2O_6 in HMF formation from cellulose at 230 °C. At the optimum condition (220 °C), HMF yields from dehydration of glucose catalyzed by H_3PO_4, CaP_2O_6 and α-$Sr(PO_3)_2$ were 9.6%, 20.0%, and 20.9%, respectively. This result revealed that both CaP_2O_6 and α-$Sr(PO_3)_2$ catalysts can effectively enhance the HMF formation when compared with H_3PO_4 in the temperature range of 200–220 °C.

It was reported that solid phosphate catalysts tend to deactivate because the phosphorus in form of a phosphate is slowly leached from the catalyst into the reaction solution.[18–20] In our reaction system tested at 230 °C, Ca and Sr leached out into the solution were determined as 8.4% and 18.9%, respectively. The effect of the leached metal species was tested in the glucose conversion in comparison with the developed heterogeneous metal at the same catalyst loading. As a result, the HMF yields (5–7%) obtained over homogeneous catalytic systems of both Sr and Ca phosphates were slightly higher than that obtained in the no-catalyst system, but lower than that achieved in the H_3PO_4-catalyzed condition. The leached Sr species gave a bit higher activity than the leached Ca one. Obviously, the heterogeneous catalysis over the phosphates provided better activity than the homogeneous ones. The results suggested that the effect of the leached metal species played a minor role on the formation of HMF.

.These results indicated that partial degradation of the metal phosphate catalysts proceeded under the hot compressed water conditions. The reaction under milder conditions would be more favorable, while development of the catalysts with lower leaching rate could be considered in future study. It is worth noting that some solvent systems have been proposed for HMF synthesis from cellulose.[21] The 4% yield of HMF was obtained from cellulose using *N*,*N*-dimethylacetamide DMA-lithium chloride LiCl as solvent and [EMIM]Cl as additive.[21] Moreover, addition of homogeneous catalysts, including $CrCl_2$, $CrCl_3$, or HCl can improve HMF yield from 4% to 54%. However, the uses of additives, solvents or ionic liquids significantly increase operating cost, and sophisticate the unit operations. Further improvement of these reaction processes to enhance the product yield and to suppress the operating cost remains a significant challenge.

In summary, the performance of calcium phosphate and α-strontium polyphosphate for conversion of fructose, glucose, and cellulose in HCW was investigated. The Ca and Sr phosphates were well-crystallized as CaP_2O_6 and α-$Sr(PO_3)_2$, respectively, while SEM and N_2 sorption analyses suggested their nonporous structures with a surface area below 0.5 $m^2\ g^{-1}$. The acid strength of both catalysts was in the range of $+3.3 \leqslant H_0 \leqslant +4.8$. The phosphates showed excellent activity in fructose and glucose dehydration,

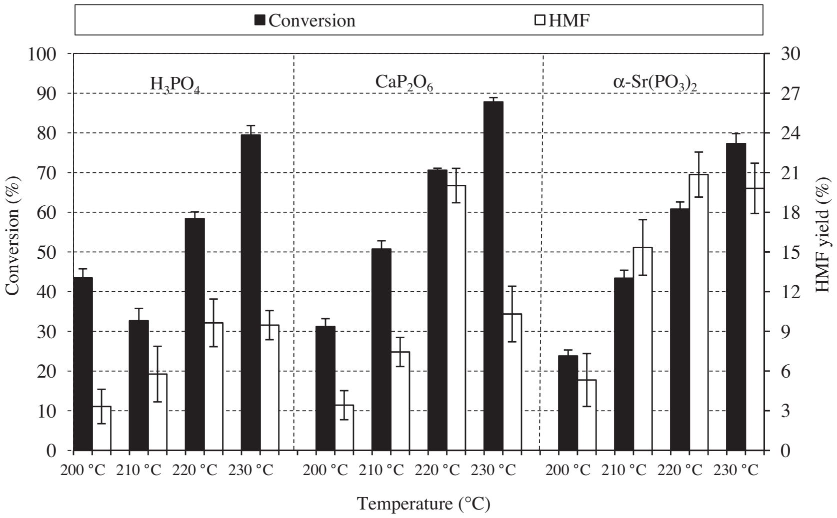

Figure 4. The effect of reaction temperature on the dehydration of glucose to HMF catalyzed by H_3PO_4, CaP_2O_6, and α-$Sr(PO_3)_2$. Reaction conditions: temperature = 200–230 °C; reaction time = 5 min; catalyst loading = 0.1 M H_3PO_4 or 1 wt.% phosphate catalyst.

giving HMF yield of 20–21% and 34–39%, respectively, while yield of glucose and HMF from hydrolysis/dehydration of cellulose were highest at 34% over α-$Sr(PO_3)_2$.

1. Experimental

1.1. Solid acid sample preparation and characterization

The alkaline earth phosphates of strontium and calcium were synthesized using conventional precipitation in acetone–water media system. Then, $CaCO_3$ or $SrCO_3$ (1.0 g) was dissolved in 5 cm^3 of 70% H_3PO_4 aqueous solution. Next, the solution was added by 30 cm^3 of acetone, and vigorously stirred for 1 h. The precipitated products were filtered and washed with acetone. After that, the obtained samples were dried in an oven overnight, and then were calcined in air at 900 °C for 3 h.

The specific surface areas of all catalysts were determined by conventional N_2 sorption at 77 K (BELSORP-max, BEL, Japan). The crystalline structure of the alkaline earth phosphate catalysts was analyzed by X-ray diffraction (XRD, Bruker D8 Advance, Germany). Morphology of compounds 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 dicinnamalactone ($pK_a = -0.3$).

1.2. Catalytic evaluation

The reactions were carried out in a batch-type reactor (SUS316 tube reactor with an inner volume of 10 cm^3). A mixture of fructose, glucose, or cellulose (0.1 g), distilled water (1 cm^3), and solid catalyst (0.01 g) was added into the above 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 of H_3PO_4 concentration. Next, the reactor was heated to 200 and 220 °C for dehydration of fructose and glucose, respectively, 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 HPLC with a Shodex RSpak KC811 column coupled with UV detector for HMF and a Shodex Sugar SP810 column coupled with reflective index (RI) detector for sugars (fructose and glucose). The amount of metal leaching in the reaction media after the reaction tests was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, JOBIN YVON HORIBA, ULTIMA 2 C).

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