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Title: Conversion of fructose, glucose and sucrose to 5-hydroxymethyl-2-furfural over meso-porous zirconium phosphate catalyst

Author: Archana Jain Andrew M. Shore Subash C. Jonnalagadda Kandalam V. Ramanujachary Amos Mugweru



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Research highlights:

- Mesoporous zirconium phosphate was used as a catalyst
- Glucose fructose and sucrose efficiently converted to HMF.
- High HMF yield up to 80% was achieved.
- Catalyst synthesized using hydrothermal method.
- Catalyst reusable after regeneration through heating.

Conversion of fructose, glucose and sucrose to 5hydroxymethyl-2-furfural over meso-porous zirconium phosphate catalyst

Archana Jain, Andrew M. Shore, Subash C. Jonnalagadda, Kandalam V. Ramanujachary and Amos Mugweru*

Department of Chemistry and Biochemistry, Rowan University, Glassboro, NJ 08028

*Corresponding Author. Tel.: +1-856-256-5454.

E-mail address: <u>mugweru@rowan.edu</u>

Abstract

5-hydroxymethyl-2-furfural (HMF) is considered an important platform chemical among other intermediates derived from biomass. In this study, we have used mesoporous zirconium phosphate as a catalyst for the conversion of sugars to HMF. The catalyst was synthesized using a hydrothermal method and was characterized using powder XRD, FT-IR spectroscopy and FESEM. The as prepared catalyst showed porous structure and a very high surface area. Mesoporous zirconium phosphate exhibited excellent catalytic activity for the formation of HMF, from fructose, glucose and sucrose. The effect of various factors such as reaction time, temperature and reaction systems on formation of HMF has been investigated.

Keywords

Mesoporous zirconium phosphate, 5-Hydroxymethyl-2-furfural, Glucose, Sucrose and Fructose.

1. Introduction

Diminishing natural recourses and their growing prices, have lead to extensive efforts focused on the wasted biomass for production of chemicals and fuels [1-4]. Biomass is inexpensive, renewable and abundant in nature. 5-hydroxymethyl-2-furfural (HMF) is considered an important signature chemical among other chemical intermediates derived from the biomass [5-7]. Other useful intermediates, including, the bio-based polymers (2,5-diformylfuran and 2,5furandicarboxylic acid), fuels (2,5-dimethylfuran) and solvents such as, levulinic acid can be prepared by the selective oxidation, reduction and rehydration of HMF respectively [8, 9]. HMF is synthesized from the dehydration of mono-/di-/polysaccharides (such as fructose, glucose, sucrose, cellobiose and cellulose etc.) [10-13]. The use of fructose as substrate is not economical because of its low availability and high cost. Glucose which is the main component of biomass has been considered more desirable substrate. The formation of HMF from glucose requires an initial isomerization to fructose, followed by the dehydration of fructose. The synthesis of HMF from hexose has been performed using a variety of acid catalysts such as inorganic materials [3, 14], organic acids [15] and metal chlorides [16], and heterogeneous catalysts e.g. zeolites [17, 18] , ion-exchange resins[19, 20], heteropoly acid salts[21] sulfated[22] and phosphoric acid treated metal oxides[23]. Extensive efforts have been made to improve the yield of HMF by adopting different kind of reaction methods and solvent systems such as ionic liquids or aqueous/bi/multiphase organic solvent systems [10, 11]. Metal phosphates (such as Al, Ti, Zr and Nb) have also been employed as heterogeneous acid catalysts for the conversion of sugars to HMF due to the presence of the Lewis (metal sites) and Brønsted (protonated phosphate group) acidic sites [24]. It has been reported that, the Lewis acidic sites on the solid catalyst, promotes the isomerization of glucose to fructose, via intermolecular hydride shift, while the Brønsted

acidic sites helps in the dehydration of fructose to HMF [25-27]. Benvenuti et. al.[28] performed a comparative study of the catalytic activity of various form of Zr-/Ti-phoshates (layered and cubic forms) for the conversion of fructose to HMF in aqueous media and suggested cubic zirconium pyrophosphate and γ -titanium phosphate as the best catalysts among the investigated samples. On the other hand, Asghari et. al. [29] investigated the catalytic performance of the crystalline and amorphous forms of zirconium phosphate under sub-critical water conditions for the dehydration of fructose to HMF. To the best of our knowledge, the use of the meso-porous zirconium phosphate as catalyst in the preparation of HMF from hexoses has not been reported so far.

In this work, the catalytic activity of mesoporous zirconium phosphate (ZrP) for the formation of HMF from fructose, glucose and sucrose was investigated. This material was prepared by hydrothermal method at low temperature using CTAB as a cationic pore directing agent. It has a mesoporous structure with a very high surface area (407 m²/g). Due to the high surface area, this catalyst exhibited excellent catalytic performance for hexose transformation to HMF with high yield. We have also studied the effect of various factors such as solvents, reaction time, temperature and reaction systems on its catalytic activity in the formation of HMF. The catalyst was regenerated by heat treatment and exhibited acceptable performance after re-use.

2. Experimental

2.1 Chemicals: All chemicals required for the synthesis of catalyst and catalytic reactions were purchased from Alfa Aesar, Acros Organics, Sigma Aldrich and BDH companies.

2.2 Catalyst synthesis: The zirconium phosphate (ZrP) catalyst was synthesized according to a literature procedure with slight modification[30]. Briefly, hydrothermal treatment involving an in-situ generated zirconium carbonate complex, di-ammonium hydrogen ortho-phosphate, and hexadecyl trimethyl ammonium bromide (CTAB) in a basic medium was carried out. CTAB is a micelle forming agent that is used in the process to add porosity to the catalyst. The white zirconium carbonate was precipitated out upon mixing of a dilute aqueous solutions of ammonium carbonate (Alfa Aesar, ACS, NH₃ 30.0 +%) (3 g dissolved in 200 mL DI H₂O) and zirconium oxychloride (Alfa Aecar, 98%) under continuous stirring. After complete precipitation, the solid residue was collected by repeated centrifugation and washings with water until the complete removal of chloride ions. The chloride free precipitate was mixed in an aqueous solution of ammonium carbonate and vigorously stirred until a clear solution was obtained. Finally, this solution was diluted to 175 mL using distilled water. A 50 ml aqueous solution of 6.5506 g di-ammonium hydrogen orthophosphate, [(NH₄)₂HPO₄] (ACS, 98% min.) was added to the clear solution at a fixed flow rate (5 ml min⁻¹) to make a 225 mL solution of 1% (w/v). The aqueous solutions containing CTAB (Amresco, high purity grade) was placed in a 1000 mL thick-wall glass bottle and stirred continuously for 12 h at room temperature, then at 80°C for 2 days and finally at 90°C for 1 day in the same glass bottle. The reaction mixture was left for another day in a teflon lined stainless steel reactor (Parr bomb) that was kept in a preheated hot air oven at 135°C. After cooling, the white precipitate reaction mass was centrifuged, washed thoroughly with distilled water and dried in a hot air oven at 80°C for 12 h. The dried samples were calcined in a high temperature furnace at 550°C for 6 h to get pure mesoporous zirconium phosphate. Synthesis was carried out using molar ratio of Zr⁴⁺/PO₄³⁻/CTAB/H₂O: 1:2:0.25:1000.

2.3 Instrumentation

Powder X-ray diffraction analysis of the catalyst was carried out using Panalytical Empyrean Diffraction System with an operating voltage set to 40 kV and current of 45 mA using Cu K α radiations ($\lambda = 1.542$ Å). X-ray diffraction patterns were recorded at 0.01 deg/min step in 5-90 degree range using 8 seconds residence time. Fourier transform infrared (FT-IR) spectra of zirconium phosphate and pyridine absorbed sample were recorded on Perkin Elmer (Model spectrum 100). The Field-emission scanning electronic microscope (FESEM) images were collected on FEI Quanta 3D FEG operated at an accelerating voltage of 5kV. The specific surface area and pore volumes were obtained by means of N₂ adsorption and desorption studies on a Nova 2200 operated at 77 K. The specific surface area was determined by using Brunauer-Emmette-Teller (BET) method and the pore volume by John-teller method. The catalyst was degassed at 300 °C for 16 h prior to the surface area measurements.

2.4 Synthesis of HMF

The reactions were performed in a thick-walled glass pressure tube. In a typical experiment, sugar, catalyst, aqueous phase (saturated NaCl solution), and diglyme were placed in the glass reactor vessel respectively. The aqueous phase and diglyme were used in the volume ratio of 1:3. The glass reactor vessel was sealed and placed in a pre-heated oil bath at a set temperature with continuous stirring. After the set time, the reaction mixture was cooled down in an ice bath and then transferred into a centrifuged tube. The reaction mixture was separated from the catalyst by centrifuging it. The solid catalyst was washed with water and acetone respectively and dried in a hot air oven at 100°C. The analysis of liquid layer was performed by means of high performance

liquid chromatography (HPLC) using a Agilent 1100 series instrument and C18 reverse phase column of dimensions 250 mm x 4.6 mm x 5.0 μ m. The product solution containing HMF was run using a mobile phase of acidic water and methanol (0.05% H₂SO₄ (10%) + MeOH (90%)) at a flow rate of 1mL min⁻¹. The HMF peak was identified by its retention time in comparison with the standard sample. The actual concentration of HMF was determined from the calibration plot (see supplementary data, Fig. S1). The results are tabulated (Table 1). The HPLC chromatograms are shown for a few selective reactions in supplementary data (Figs. S2-S4). The proton NMR of the crude product in the case of the dehydration reaction of fructose to HMF (entry # 3 in table 1) is also shown as a reference in fig. S5.

3. Results and discussion

3.1 Catalyst characterization

The powder XRD pattern of the calcined ZrP sample shows two broad peaks in 20 ranges of 10-40° and 40-70° and suggests its amorphous nature (Fig. 1a). The FT-IR spectra of the sample before and after calcination are shown in Fig. 2a. The as-synthesized sample exhibits a broad peak at 1000-1200 cm⁻¹ that is due to $-PO_4$ stretching vibration and shifts towards higher wave numbers (ca. 55-65 cm⁻¹) after calcination. The bands at 3375 and 1630 cm⁻¹ are attributed to the asymmetric OH stretching and bending of water molecule, respectively. The bands at 1471 and 2800-3000 cm⁻¹ are due to the C-H stretching of the surfactant that disappear after calcinations. A similar pattern of powder XRD and FT-IR of mesoporous zirconium phosphate has been reported by Sinhamahapatra *et al* [31]. The surface acidity of ZrP has been determined by FT-IR using pyridine as a probe molecule. Pyridine forms pyridinium ions with proton (Brønsted acid sites) and is coordinated to electron-deficient metal centers (Lewis acid centers)[31]. Fig. 2b shows the FT-IR of zirconium phosphate before and after adsorption of pyridine. The band at

~1545 cm⁻¹ is assigned to pyridinium ion, confirming presence of Brønsted acid sites. The Brønsted acidity arises as a result of presence of geminal P(OH) groups [32]. A peak at around ~1445 cm⁻¹ is due to the pyridine attached to a Lewis acid center. The band at 1490 cm⁻¹ is a combination band between two separates bands at 1545 and 1445 cm⁻¹, corresponding to Brønsted and Lewis acid sites respectively.

The specific surface area of calcined mesoporous zirconium phosphate was found to be 407 m^2/g , as analyzed, using multilayer BET method. Figure 1b shows the nitrogen adsorption-desorption isotherm of calcined m-ZrP. The isotherm of ZrP is of type IV according to IUPAC which is of characteristics of mesoporous materials. The pore size distribution plot (Fig. 1b inset) derived from this isotherm using non local density functional theory (NLDFT) show a very narrow pore size distribution. The field-emission scanning electronic microscopic images of calcined zirconium phosphate reveals spherical nature as well as agglomeration of the particles containing rough surfaces (Fig. S6).

3.2 Catalytic reactions

Previous reports indicate, mesoporous ZrP as an efficient catalyst for the xylose conversion to furfurals as a result of a large surface area, as well as presence of Lewis and Bronsted acidic sites [33]. In the present study, the catalytic activity of synthesized mesoporous ZrP was examined in the conversion of fructose, glucose and sucrose to HMF under various reaction conditions. In the first set of experiments, the effect of solvents on HMF yield was investigated. The dehydration of fructose was performed in different solvent systems under conventional refluxing conditions. The following reaction conditions were used: 1000 mg fructose, 500 mg ZrP catalyst, water/organic solvent (saturated with NaCl, 1:3 v/v) (40 mL), and at 150 °C for 4 h. The highest

HMF yield was obtained in water-dyglyme solvent system (Fig. 3). We also compare the yield of HMF from reactions done in different conditions. Conventional refluxing system, sealed reactor system were compared while studying the conversion of fructose to HMF. The following reaction conditions were used. 100 mg fructose, 50 mg ZrP catalyst, water/diglyme solvent (1:3 v/v, saturated with NaCl), and at 150 °C. The yield of HMF was found to be 80% in just 1 h in the case of reaction done in a sealed reactor (Entry #3 in table 1), as compared to 61% HMF yield in 4 h from the reaction done under refluxing conditions (Entry #20 in table 1). It can be clearly seen that the heating in a sealed reactor helps in maximizing the HMF yield and also reduces the reaction time.

In further study, the effect of catalyst and salt as co-catalyst on the HMF yield was investigated. The reactions were performed in water-diglyme solvent system in presence of both catalyst ZrP and co-catalyst NaCl or in absence of one of them using fructose, glucose, and sucrose as substrates (Entries #3, 8, 9, 12-14, and 17-19 in table 1 respectively) in a sealed reactor. A higher HMF yield as measured using HPLC was observed, when the catalyst and co-catalyst were used together (Fig. 4).

Table 1	: HMF	synthesis	from f	fructose,	glucose	and	sucrose	in a	sealed	reactor	using	ZrP
catalyst												

Entry	Substrate (mg)	Catalyst	Solvents	Time	T(°C)	HMF yield
		(mg)	(4 mL)	(h)		(mol %)
1	Fructose, 100	ZrP, 50	H ₂ O-diglyme	2	150	77
2	Fructose, 100	ZrP, 50	H ₂ O-diglyme	1.5	150	78
3	Fructose, 100	ZrP, 50	H ₂ O-diglyme	1	150	80
4	Fructose, 100	ZrP, 50	H ₂ O-diglyme	0.5	150	50

5	Fructose, 100	ZrP, 50	H ₂ O-diglyme	1	180	73
6	Fructose, 100	ZrP, 50	H ₂ O-diglyme	1	120	43
7	Fructose, 100	ZrP, 50	H ₂ O-diglyme	1	100	38
8	Fructose, 100	ZrP, 50	H ₂ O-diglyme ^a	1	150	36
9	Fructose, 100	-	H ₂ O-diglyme	1	150	7
10	Glucose, 100	ZrP, 50	H ₂ O-diglyme	2.5	150	45
11	Glucose, 100	ZrP, 50	H ₂ O-diglyme	2	180	61
12	Glucose, 100	ZrP, 50	H ₂ O-diglyme	3	180	63
13	Glucose, 100	ZrP, 50	H ₂ O-diglyme ^a	2	180	31
14	Glucose, 100	-	H ₂ O-diglyme	2	180	3
15	Glucose, 100	ZrP, 50	H ₂ O-diglyme ^b	2	180	56
16	Sucrose, 100	ZrP, 50	H ₂ O-diglyme	1	180	52
17	Sucrose, 100	ZrP, 50	H ₂ O-diglyme	2	180	53
18	Sucrose, 100	ZrP, 50	H ₂ O-diglyme ^a	2	180	22
19	Sucrose, 100	X	H ₂ O-diglyme	1	180	1
20 ^c	Fructose, 1000	ZrP, 500	H ₂ O-diglyme	4	150	61

 H_2O -diglyme = 1:3 (v/v) saturated with salt (NaCl); ^{*a*} without salt (NaCl); ^{*b*} solvent = 2 mL;

^c reaction done in RB flask equipped with refluxing condenser using 40 mL H₂O-diglyme solvent mixture.

In the absence of co-catalyst (NaCl), HMF yield, reduced by ~30-50%. The addition of sodium chloride to the aqueous phase leads to increased HMF yields because of the improvement of the partitioning of HMF into the extracting phase by means of the salting out effect [34]. In blank reaction (without catalyst), very low yield of HMF was observed (Entries #8, 13 and 19 in table

The effects of reaction time on HMF yield were also studied for the conversion of fructose to HMF under the same reaction conditions in sealed reactor (Entries # 1-4 in table 1). Fig. 5 shows the effect of time on the HMF yield. In prolonged reaction time, a slight decrease in the HMF yield was observed, most likely due to the minor transformation of HMF to other products[35]. The effect of reaction temperature, on the HMF yield was also investigated. The yield obtained in temperature range from 100 to180 °C using ZrP (50 mg) as solid catalyst are shown in table 1. It was found that the HMF yield increased on increasing temperature from 100 °C to 150 °C (Fig. 6). Further increase in temperature decreases the HMF yield drastically. This may be attributed to the side reactions occurring at higher temperatures.

The reusability of the catalyst was tested for the conversion of fructose to HMF under the conditions of 100 mg fructose, 50 mg ZrP catalyst, water/diglyme solvent (saturated with NaCl, 1:3 v/v) (4 mL), and at 150 °C for 1 h in a sealed glass reactor. The catalyst was collected by repeated centrifugation and washing with water and acetone for several times after each cycle. The catalyst as obtained was brownish in color, due to deposition of organic by-products. The catalyst was successfully regenerated by heating at 500 °C for 2 h in air in a furnace and then used for the fresh reaction. As shown in Fig. 7, the catalyst was re-used for five times, and only a slight decrease in HMF yield was observed.

4. Conclusions

In this study, the catalytic activity of synthesized ZrP was examined in the conversion of fructose, glucose and sucrose to HMF under various reaction conditions. The effect of various factors such as reaction time, temperature and reaction systems on HMF yield was also investigated. It was found that the heating for longer time and at high temperature had negative

impact on HMF yield due to the formation of side products. The catalyst recycled five times showed negligible reduction in activity as observed in HMF yield.

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References:

- M. A. Rubio Rodríguez, J. D. Ruyck, P. R. Díaz, V. K. Verma, S. Bram, *Appl. Energ.*, 88 (2011) 630-635.
- [2] W. P. Nel, C. J. Cooper, *Energ. Policy*, *37* (2009) 166-180.
- [3] Y. Román-Leshkov, J. N. Chheda, J. A. Dumesic, *Science*, *312* (2006) 1933-1937.
- [4] C. H. Christensen, J. Rass-Hansen, C. C. Marsden, E. Taarning, K. Egeblad, *ChemSusChem*, 1 (2008) 283-289.
- [5] J. Lewkowski, *Arkivoc, 1* (2001) 17-54.
- [6] A. Corma, S. Iborra, A. Velty, *Chem. Rev.,* 107 (2007) 2411-2502.
- [7] S. P. Simeonov, C. A. M. Afonso, J. Chem. Educ., 90 (2013) 1373-1375.
- [8] A. A. Rosatella, S. P. Simeonov, R. F. M. Frade, C. A. M. Afonso, *Green Chem.*, 13 (2011) 754-793.
- [9] S. Dutta, S. De, B. Saha, ChemPlusChem, 77 (2012) 259-272.
- [10] L. Hu, G. Zhao, W. Hao, X. Tang, Y. Sun, L. Lin, S. Liu, *RSC Adv.*, 2 (2012) 11184-11206.
- [11] X. Tong, Y. Ma, Y. Li, Appl. Catal. A-Gen., 385 (2010) 1-13.
- [12] J. Shi, H. Gao, Y. Xia, W. Li, H. Wang, C. Zheng, *RSC Adv.*, *3* (2013) 7782-7790.
- [13] M. Yabushita, H. Kobayashi, A. Fukuoka, Appl. Catal. B- Environ., 145 (2014) 1-9.
- [14] B. F. M. Kuster, H. S. van der Baan, *Carbohyd. Res., 54* (1977) 165-176.
- [15] W. N. Haworth, W. G. M. Jones, J. Chem. Soc. (Resumed), (1944) 667-670.
- [16] H. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, Science, 316 (2007) 1597-1600.
- [17] C. Moreau, R. Durand, S. Razigade, J. Duhamet, P. Faugeras, P. Rivalier, P. Ros, G. Avignon, *Appl. Catal. A-Gen.*, 145 (1996) 211-224.
- [18] K.-i. Shimizu, R. Uozumi, A. Satsuma, *Catal. Commun.*, *10* (2009) 1849-1853.
- [19] Y. Nakamura, S. Morikawa, B. Chem. Soc. Japan, 53 (1980) 3705-3706.
- [20] X. Qi, M. Watanabe, T. M. Aida, R. L. Smith, *Ind. Eng. Chem. Res.*, 47 (2008) 9234-9239.
- [21] C. Fan, H. Guan, H. Zhang, J. Wang, S. Wang, X. Wang, *Biomass and Bioenerg.*, 35 (2011) 2659-2665.
- [22] H. Yan, Y. Yang, D. Tong, X. Xiang, C. Hu, *Catal. Commun.*, *10* (2009) 1558-1563.
- [23] F. Yang, Q. Liu, X. Bai, Y. Du, *Bioresource Technol.*, 102 (2011) 3424-3429.
- [24] V. V. Ordomsky, V. L. Sushkevich, J. C. Schouten, J. van der Schaaf, T. A. Nijhuis, *J. Catal., 300* (2013) 37-46.
- [25] Y. Román-Leshkov, M. Moliner, J. A. Labinger, M. E. Davis, *Angew. Chem. Int. Ed.,* 49 (2010) 8954-8957.

- [26] E. Nikolla, Y. Román-Leshkov, M. Moliner, M. E. Davis, ACS Catal., 1 (2011) 408-410.
- [27] K. Yamaguchi, T. Sakurada, Y. Ogasawara, N. Mizuno, *Chem. Lett., 40* (2011) 542-543.
- [28] F. Benvenuti, C. Carlini, P. Patrono, A. M. Raspolli Galletti, G. Sbrana, M. A. Massucci, P. Galli, *Appl. Catal. A-Gen.*, *193* (2000) 147-153.
- [29] F. S. Asghari, H. Yoshida, *Carbohyd. Res., 341* (2006) 2379-2387.
- [30] A. Sinhamahapatra, N. Sutradhar, B. Roy, A. Tarafdar, H. C. Bajaj, A. B. Panda, *Appl. Catal. A-Gen., 385* (2010) 22-30.
- [31] D.K. Chakrabarty, B. Viswanathan, *Heterogeneous Catalysis, New Age International Publishers*, (2008) 213.
- [32] A. Corma, *Chem. Rev., 95* (1995) 559-614.
- [33] L. Cheng, X. Guo, C. Song, G. Yu, Y. Cui, N. Xue, L. Peng, X. Guo, W. Ding, *RSC Adv., 3* (2013) 23228-23235.
- [34] Y. Román-Leshkov, J. Dumesic, *Top. Catal.*, *52* (2009) 297-303.
- [35] X. Qi, M. Watanabe, T. M. Aida, J. R. L. Smith, *Green Chem.*, 11 (2009) 1327-1331.

Figure captions

Figure 1: (a) Powder X-ray diffraction pattern and (b) N₂ adsorptin-desorption isotherm and corresponding pore size distribution curve (inset) of calcined msoporous zirconium phosphate

Figure 2: FT-IR spectra of (a) as synthesized and calcined m-ZrP and, (b) calcined m-ZrP before and after adsorption of pyridine

Figure 3: Effect of different biphasic solvents on HMF yield

Figure 4: Effect of catalyst and co-catalyst on HMF yield

Figure 5: Effect of the reaction time on HMF yield

Figure 6: Effect of the reaction temperature on HMF yield

Figure 7: Re-use of the catalyst for the conversion of fructose to HMF (Reaction conditions: fructose: 100 mg, catalyst ZrP: 50 mg; H₂O-diglyme: 4 mL in volume ratio of 1:3, saturated with NaCl; time:1 h; and temp.: 150°C; sealed reactor)





















