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Dehydration of fructose to 5-hydroxymethylfurfural in sub-critical water over heterogeneous zirconium phosphate catalysts

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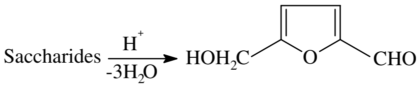
Abstract—Dehydration of fructose to 5-hydroxymethylfurfural in a batch-type process with sub-critical water (sub-CW) was performed in the presence of different laboratory-made zirconium phosphate solid acids at 240 °C. A direct relation was found between increasing the crystallinity and decreasing the surface area of solid acids. However, irrespective of the different surface areas, similar catalytic behaviors were observed. Meanwhile, calcination of the samples showed no improvement in the activity of the solid acids. In the presence of the amorphous form of zirconium phosphate, about 80% of fructose was decomposed in sub-critical water at 240 °C after 120 s, and the selectivity of the dehydration reaction of fructose to 5-hydroxymethylfurfural rose to 61%. No rehydration products were identified. Soluble polymers and furaldehyde were the only major and minor side products found, respectively. Finally it was found that zirconium phosphate solid acids were stable under sub-CW conditions, and they can easily be recovered without changing their catalytic properties.

Keywords: Sub-critical water; Solid acid; Zirconium phosphate; Fructose; Dehydration; 5-Hydroxymethylfurfural

1. Introduction

In recent years, attention has been focused on the production of various chemical compounds by using sub- and supercritical water systems as an alternative technique to conventional methods.[1,2] Within this framework, sub-critical water (hereafter called sub-CW) is used for the conversion of monosaccharides (and also oligo- and polysaccharides that can yield hexoses on hydrolysis) as major renewable raw materials for industrial chemicals and related materials. In particular this process is used for the conversion to the petrochemical-like compound, 5-hydroxymethylfurfural[3–5] (hereafter called HMF). HMF is a valuable chemical feedstock that has numerous industrial applications, especially in polymer chemistry.[6] Seri and Ishida[7] have correctly labeled it as a 'very expensive chemical'. This compound is synthesized via the acid-catalyzed dehydration of saccharides in water and/or organic solvents mixture (Scheme 1). Since Düll and Kiermeyer independently introduced a method of synthesis of HMF in 1895,[8] many researchers reported different preparation methods along with application of homogeneous and heterogeneous acids both in aqueous and non-aqueous media. Some examples are the following: mineral acids[9–11] (H_2SO_4, HCl, and H_3PO_4), organic acids[12–16] (oxalic, levulinic, *p*-toluenesulfonic, and maleic acids), Lewis acids ($ZnCl_2$, $AlCl_3$, and BF_3), salts (NH_4SO_4/SO_3, pyridine/PO_4^{3-}, pyridine/HCl, and also Al, Th, Zr, lanthanide ions),[17–20] and solid catalysts[6,21–24] (ion-exchange resins, zeolites, and metal(IV) phosphates), which were all commonly used in the production of HMF.



Scheme 1. Dehydration of saccharides to HMF.

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Application of homogenous acids, however, are typically associated with the problems of high toxicity, corrosion, catalyst waste, use of large amounts of catalyst, and the difficulty of separation and recovery. Heterogeneous acids, on the other hand, overcome most disadvantages of homogeneous acids as they offer the advantages of easy separation from reaction products, recycling, and higher selectivities than homogeneous ones.[25]

From another point of view, it is obvious that aqueous-phase reactions have interesting advantages: Water is the cheapest, non-toxic, non-flammable, clean solvent, which increases the economic feasibility of the process. However, there are quite a few numbers of solid acids that are acceptable in terms of their activity, stability, and insolubility for the reactions in aqueous media and particularly in water at high temperature and pressure. In fact most solid acids lose their catalytic activities in aqueous solutions.[25] Zirconium phosphate (hereafter called ZrP) solid acids possess properties that make them compatible, not only with the reactions in which water is generated, but also in all reactions with aqueous media. ZrP solids have been primarily used as ion exchangers.[26] However, the use of these solids as catalysts in various reactions such as dehydration, isomerization, polymerization, and alkylation has received considerable attention during the last few years,[27–29] as attested to by the numbers of papers and patents that have recently been published. In the presence of different ZrP solids, the dehydration of alcohols,[30] esterification of acetic acid with ethanol,[31] oxidation of propene,[32] and dehydration of cyclohexanol[28] have been widely studied.

For reactions under sub-CW conditions, and particularly for reactions of saccharides, the application of only a few homogeneous and heterogeneous catalysts has been reported.[3–5,33] In previous work,[16] we studied the effect of various homogeneous acids in the range of pH 1.5–5 on dehydration of fructose to HMF under sub-CW conditions. The application of ZrP solids (or generally metal(IV) phosphates salts) in the reaction of saccharides is limited to a few available academic and patent reports. Nakamura[22] in a patent used normal temperature and pressure for the preparation of HMF from hexoses in DMSO with ZrP catalyst and got a maximum yield of 81% for HMF after 3 h of reaction at 140 °C. A catalytic activity equal to a turnover frequency (TOF) of $0.23\ \text{g}\,\text{g}^{-1}\,\text{h}^{-1}$ was obtained. Benvenuti et al.[34] studied the application of various zirconium and titanium phosphate salts in dehydration of fructose and inulin to HMF in aqueous media under normal temperature and pressure conditions in batch and continuous systems at 110 °C. They obtained TOF of about $1.62\ \text{g}\,\text{g}^{-1}\,\text{h}^{-1}$ and almost complete selectivity toward HMF. In titanium phosphates under the same conditions, the TOF of about $1.08\ \text{g}\,\text{g}^{-1}\,\text{h}^{-1}$, and good selectivity to HMF was reported. Inomata and co-workers[33] studied the comparison of the homogeneous acid and base (H_2SO_4 and NaOH) and two metal oxides as an example of a heterogeneous acid and base (TiO_2, ZrO_2) for glucose reactions under sub-CW conditions at 200 °C toward isomerization and dehydration of glucose. They observed isomerization in the reaction of glucose by NaOH and ZrO_2 by the basic catalysts, and a dehydration reaction by H_2SO_4 and TiO_2 by the acidic catalysts.

The well-matched properties of ZrP solids as catalysts with aqueous-phase reactions make these compounds attractive for use under sub-CW conditions. In the present work, we studied the applicability of ZrP solid acids under sub-CW conditions as alternatives to homogeneous acids for dehydration of fructose to HMF.

2. Experimental

2.1. Materials

Zirconium chloride (Chameleon reagent, 98%) was used as the zirconium source. All other reagents, phosphoric acid (85%), HCl (35%), HF (46–48%), MeOH (HPLC grade), D-fructose (99%), D-glucose (99%), 5-hydroxymethylfurfural (99%), furaldehyde (99%), levulinic (95%), and formic (99%) acids were purchased from Wako Pure Chemical Industries (Japan). All reagents were used without purification.

2.2. Solid acid sample preparation

Schematic preparation procedure is shown in Figure 1. The catalyst was prepared by modifying the procedure given by Clearfield and Stynes.[35] The best results were obtained as follows: $ZrCl_4$ (0.5 g, 2.15 mmol) as a zirconium precursor salt was dissolved in HCl (3 mL, 2 N). H_3PO_4 (3 mL, 7 N) was then added while the solution was stirred at room temperature. The gel that was produced was then refluxed in about 10 N H_3PO_4 until

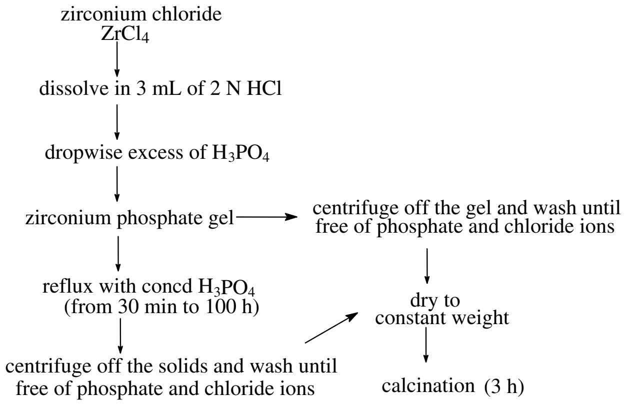

Figure 1. Schematic representation of the preparation method.

crystalline zirconium phosphate (ZrP) was produced. The crystalline ZrP solid can be made with any degree of crystallinity by varying the refluxing period.[36] The precipitated solid was washed with 2 N H_3PO_4 and then with distilled water until the pH reached a constant value (pH ~ 4) and until free of phosphate and chloride ions. Thereafter the sample was dried at 70 °C for 72 h and finely crushed. Finally, for calcination to occur, the samples were heated, followed by thermal treatment at 300 and 600 °C for 3 h.

2.3. Characterization of zirconium phosphates

Surface areas were measured by adsorption of nitrogen gas at −196 °C (Belsorp 18plus-T-SP, Japan). Before measurements, all samples were evacuated at 70 °C for 9 h. The surface areas were determined using the BET equation. The mercury porosimetry technique (Pascal 140 and 240, Thermo Finnigan) was used to measure the pore size distribution of ZrP solids.

Elemental analysis of phosphate and zirconium was carried out using an induced coupled plasma (ICP) atomic emission spectrophotometer (SPS-7800 Plasma spectrometer, Seiko, Japan). The composition of solids was determined as follows: about 5–7 mg of the sample was dissolved in 2 mL of 0.2 N of HF in a PVC flask. It was then diluted to 50 mL, and zirconium and phosphate contents were determined by ICP.

2.4. Catalytic dehydration reaction of fructose

A stainless steel tube (SUS 316, 8 mm i.d. and total volume of 7.7 mL) and a Swagelok fitting (purchased as from Swagelok AG, Switzerland) were used for batch-type sub-CW experiments at 240 °C. The typical procedure was as follows: fructose (0.05 g), catalyst (0.01–0.05 g), and water (5.5 g) were poured into the reactor. After the air in the reactor was replaced with argon, it was capped tightly and immersed in a salt bath (Thomas Kagaku Co. Ltd.) preheated to 240 °C. The reaction was allowed to proceed for a given reaction time. The reactor was shaken before and also during immersion in the salt bath in order to avoid settling of the catalyst particles to the bottom, which inhibits accessibility for the dissolved reactant. The reactor was then removed from the salt bath and quickly quenched in a water bath at ambient temperature. The pressure inside the reactor (3.35 MPa at 240 °C) was estimated from a steam table.[37] The sample after reaction was diluted to 50 mL with distilled water and analyzed for HMF, remaining fructose, and other byproducts.

2.5. Analysis

The products of the sub-CW reaction were analyzed by HPLC using two Varian ProStar210 solvent delivery modules with a CSPAK narrow-bore column C_{18} (2.1 × 100 mm) coupled with a pulsed amperometric (PDA) detector (Varian PDA 330 Detector), which was set to 284 nm. Gradient elution program at 0.1 mL/min flow rate was used as below:

Time (min)	% of Mobile phase A (1% aq solution of HOAc)	% of Mobile phase B (MeOH)
0	85	15
10:00	74	26
15:00	2	98
53:00	2	98
55:00	85	15
73:00	85	15

In order to identify the presence of organic acids, an HPLC instrument using Shimadzu LC-10AD VP pumps with two serial ion-exclusion chromatography columns (Shim-pack SCR-102H, 8 × 300 mm) and post-column pH-buffered electroconductivity detection (Shimadzu CDD-6A) was used. The mobile phase was 5 mM of *p*-toluenesulfonic acid solution at a flow rate of 0.8 mL/min. A mixture of 5 mM of *p*-toluenesulfonic acid and 100 mM of EDTA was used as the post-column reagent at a flow rate of 0.8 mL/min. The column temperature was kept at 40 °C. Two serial size-exclusion chromatography columns (Shodex-sugar KS 804 and KS801, 8 × 300 mm) in an HPLC using a Jasco PU-2080 plus a pump coupled with a refractive index detector (RI 2031 plus) were used for quantitative analysis of products that were undetectable by the UV detector. The HPLC was operated at an oven temperature of 30 °C and 0.4 mL/min flow rate of water as the mobile phase. The total organic carbon (TOC) concentration of samples was measured using a TOC analyzer (Shimadzu TOC-500). To heat the samples, a furnace thermoregulated within ±1 °C was used. A Horiba f-23 digital pH meter was used for pH measurements.

The conversion, selectivity, absolute yield, and turnover frequency (TOF) were calculated by Eqs. 1–4, respectively:

$$\text{conversion} = \frac{C_{\text{substrate(ini)}} - C_{\text{substrate}}}{C_{\text{substrate(ini)}}} \tag{1}$$

$$\text{selectivity} = \frac{C_{\text{product}}}{C_{\text{substrate(ini)}} - C_{\text{substrate}}} \tag{2}$$

$$\text{absolute yield} = \frac{C_{\text{product}} \times \text{MW}_{\text{substrate}}}{C_{\text{substrate(ini)}} \times \text{MW}_{\text{product}}} \tag{3}$$

$$\text{Turnover frequency (TOF)} = \frac{\text{(g of) HMF}}{\text{(g of) catalyst} \times \text{residence time (h)}} \tag{4}$$

3. Results and discussion

3.1. Properties of solid acids

Table 1 shows the surface area, weight loss by heating, and phosphate-to-zirconium molar ratio for a series of ZrP solids that were prepared in this work. The initially prepared solid acid, ZrP (0:0), had an amorphous structure.[31] It has been previously shown that amorphous forms of ZrP solids could change to semi-crystalline and crystalline forms by refluxing in concentrated phosphoric acid, while increasing with refluxing time.[26] Therefore, in Table 1 the crystallinity increased from entry A1 toward F1. All the prepared samples, including the amorphous to crystalline forms, were calcined at two temperatures, 300 and 600 °C for 3 h. The data for the calcined samples are also shown in Table 1 (A2–3 to F2–3).

The experimental results showed that the surface area decreased almost linearly by refluxing time and/or by heat treatment (Table 1). These results are quite similar to that already reported by Thakur and Clearfield.[29] The effect of reflux was greater than heat treatment on the surface area of the solid samples. By increasing the crystallinity, the surface area decreased. Therefore, with respect to the data of surface areas, it can be realized that both refluxing and calcination may increase the crystallinity of solids toward higher crystalline forms. On the other hand, the results of Table 1 showed that calcining has a more noticeable effect on the amorphous forms (i.e., on A1 and A3 in Table 1) than on the higher crystalline forms (i.e., on F1 and F3 in Table 1).

Average weight losses by the calcination at 300 and 600 °C were 7.9 ± 1% and 11.6 ± 0.2% (A2 to F2 and A3 to F3 in Table 1), respectively. These are ascribed to the disappearance of crystalline water and condensation of hydroxyl groups. It seems at 300 °C crystalline water was lost from molecules, and at 600 °C crystalline water-loss and condensation reactions of hydroxyl groups occurred.[38]

The phosphate-to-zirconium ratio was close to 2 (1.8–2) in all samples (see Table 1), which is relevant to its basic formula $Zr(O_3POH)_2{\cdot}nH_2O$, where n depends on the drying method and degree of crystallinity.[26] As shown in Table 1, a small deviation from the ratio 2 was obtained for these samples. However, in general, the crystals obtained after refluxing have approximately the same composition as the amorphous sample.

Based on the IUPAC classification on adsorption isotherms, from Figure 2 it can be found that the prepared samples were non-porous or macroporous structures.[39]

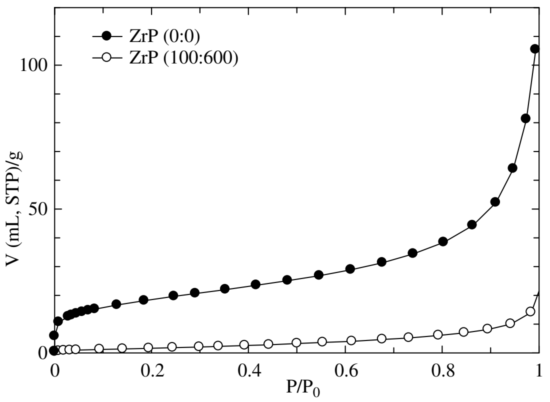

Figure 2. Typical adsorption isotherm of N_2 on ZrP salts, $T = -196$ °C.

Table 1. Properties of various prepared zirconium phosphate solids

Entry		Solid acid	Surface area, m^2/g (BET)	wt% loss	P/Zr (molar ratio)
A	1	ZrP (0[a]:0[b])	63.6	—	1.8
	2	ZrP (0:300)	54.4	7.9	1.8
	3	ZrP (0:600)	43.8	11.7	1.8
B	1	ZrP (0.5:0)	38.1	—	1.8
	2	ZrP (0.5:300)	32.4	7.9	1.8
	3	ZrP (0.5:600)	26.2	11.2	1.8
C	1	ZrP (1:0)	35.7	—	1.9
	2	ZrP (1:300)	24.6	8.0	1.9
	3	ZrP (1:600)	23.4	11.8	1.9
D	1	ZrP (3:0)	19.8	—	1.9
	2	ZrP (3:300)	18.7	7.9	1.9
	3	ZrP (3:600)	16.5	11.9	1.9
E	1	ZrP (10:0)	13.3	—	1.9
	2	ZrP (10:300)	12.5	8.1	1.9
	3	ZrP (10:600)	9.7	11.6	1.9
F	1	ZrP (100:0)	8.8	—	1.9
	2	ZrP (100:300)	6.8	7.8	2.0
	3	ZrP (100:600)	6.7	11.5	2.0

[a] Reflux time of the zirconium phosphate gel (h).

[b] Calcination temperature [°C] (0 means no calcination).

Furthermore the mercury porosimetry technique has been used in order to understand the size of the pore of the samples (in the case of macroporous). The amorphous and crystalline forms of ZrP (0:0) and ZrP (100:600) showed different pore sizes and distribution (see Fig. 3a and b), respectively. Specific pore volume decreased with increasing crystallinity, and the crystalline form had a narrow range of pore distribution compared to the amorphous one. However, it was found that for all solid samples, their volumes of macroporous were small.

In this work we investigated the possibility of using these solid acids as catalysts under sub-CW conditions. Extensive work has been done to elucidate the nature, crystallinity, and physicochemical properties of these solids in detail elsewhere.[40,41]

3.2. Catalytic activities of prepared solid acids under sub-CW conditions

From the catalytic dehydration reaction of fructose, we obtained some information on compatibility, activity, selectivity, and other relevant information of ZrP solid acids under the sub-CW conditions.

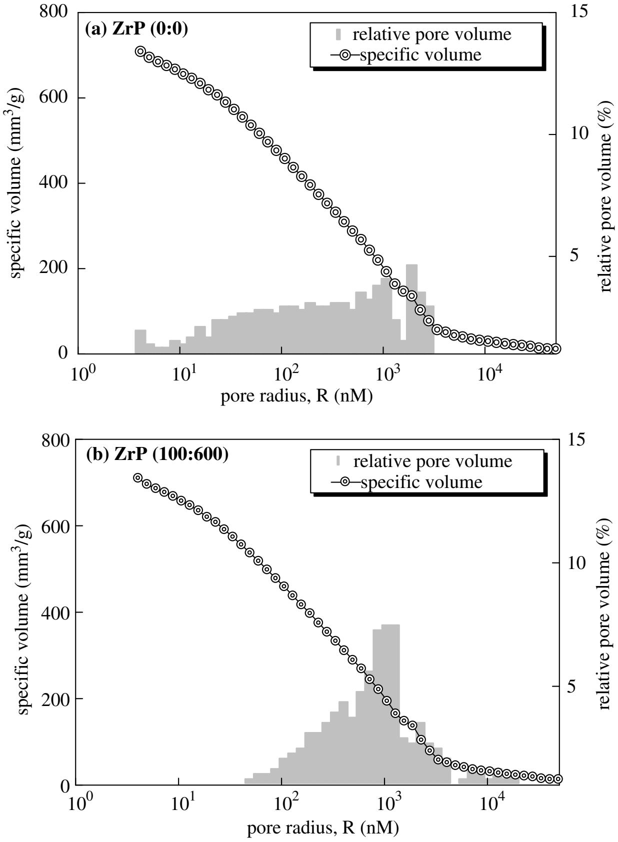

Figure 3. Typical pore-size distribution curves determined by mercury intrusion porosimetry on (a) ZrP (0:0) and (b) ZrP (100:600) solids.

3.2.1. Control experiments for catalytic activity. Primary experiments were done with and without the catalyst in order to demonstrate the existence of catalytic activity of these solid acids under the sub-CW conditions. Figure 4 shows the time course for the production yields of HMF from fructose with or without the solid acid catalyst [ZrP (0:0)] under the sub-CW conditions at 240 °C. Fructose was dehydrated to HMF, even in the absence of catalyst. With increasing sub-CW temperature, the production yield of HMF increased to 120 s. Afterward the yield of HMF decreased. This may be caused by decomposition and polymerization of HMF. It is clear that ZrP (0:0) acted as a catalyst because the yield increased about three times compared to the non-catalytic condition.

3.2.2. Effect of properties of various solid acids on dehydration reaction. In general, the catalytic properties of the solid acids depend on the method of precipitation, degree of crystallinity, calcination temperature, and other physicochemical parameters. Thus, in order to test the effect of the structure of various ZrP solids made in this work in the sub-CW reaction, a series of reactions were carried out for comparison by application of the solid acids under the same reaction conditions (residence time of 120 s, temperature of 240 °C, and catalyst-to-fructose ratio of 1:2). The experimental results, along with the results of the controlled reaction (reaction without catalyst), are summarized in Table 2. The results are given by conversion of fructose, selectivity to HMF, furaldehyde, and soluble polymers, and absolute yield of HMF. Soluble polymers could not be quantitated; therefore, their selectivities were calculated by difference, which attributed to the lost amounts in the decomposition reaction of fructose.

In the absence of catalysts, fructose conversion, and selectivity to HMF were lower than those with ZrP solid

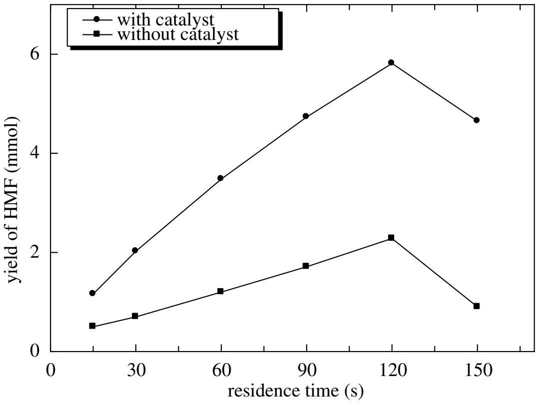

Figure 4. HMF production from dehydration of 1% solution of fructose under sub-CW conditions at 240 °C and 3.35 MPa, as function of time, in the presence and absence of amorphous form of zirconium phosphate.

Table 2. Catalytic activities of various zirconium phosphates in the dehydration of fructose (1 wt % aq solution) at 240 °C, 3.35 MPa, 120 s, with an initial catalyst-to-fructose ratio of 1:2 by weight

Entry		Catalyst	Conversion (%)	Selectivity to (%)			Absolute yield of HMF (%)
				HMF	FA[a]	Soluble polymers[b]	
G	1	ZrP (0:0)	80.6	61.3	2.2	36.5	49.4
	2	ZrP (0:300)	78.4	56.2	1.9	41.9	44.1
	3	ZrP (0:600)	77.1	52.1	1.9	46.0	40.7
H	1	ZrP (0.5:0)	80.9	62.1	2.4	35.5	50.2
	2	ZrP (0.5:300)	74.7	56.8	2.2	41.0	42.5
	3	ZrP (0.5:600)	72.2	51.4	1.9	46.7	37.2
I	1	ZrP (1:0)	79.1	59.3	2.2	38.5	46.9
	2	ZrP (1:300)	76.2	56.6	2.2	41.2	43.2
	3	ZrP (1:600)	73.7	50.5	1.9	47.6	37.2
J	1	ZrP (3:0)	79.2	62.3	2.3	35.4	49.4
	2	ZrP (3:300)	72.5	57.4	2.2	40.4	41.7
	3	ZrP (3:600)	70.9	51.7	1.8	46.5	36.6
K	1	ZrP (10:0)	79.7	62.0	2.4	35.6	49.4
	2	ZrP (10:300)	68.7	53.9	2.2	43.9	37.0
	3	ZrP (10:600)	67.2	47.2	1.6	51.2	31.7
L	1	ZrP (100:0)	81.3	60.9	2.1	37.0	49.6
	2	ZrP (100:300)	67.6	54.2	1.9	43.9	36.7
	3	ZrP (100:600)	65.6	45.3	1.5	53.2	29.7
M		Control[c]	59.1	31.8	1.1	67.1	18.6

[a] Furaldehyde.

[b] Amounts of soluble polymers calculated by difference.

[c] Reaction carried out in the absence of catalyst.

acids under the same experimental conditions (Table 2). With application of the amorphous form of catalyst, maximum conversion of fructose, about 80%, was observed, and the best selectivity of HMF was obtained at about 61%. Only 2.2% of selectivity was found for the furaldehyde (see Table 2, G1). The refluxing time and consequent degree of crystallinity, as well as the surface area of solid acids, showed no increasing effects on conversion of fructose and selectivity of HMF. (See Table 1 for surface areas and Table 2, G–L.) It has already been reported that there is a close relationship between surface area, which corresponds to hydroxyl groups of surface, and catalytic activity of ZrP solids.[28] On the other hand, under the normal reaction conditions, it has been thought that the decrease of catalytic activity is attributed to the decrease in surface area. Therefore, it has been reported that the surface areas of the ZrP solid acids were of prime importance in assessing their behavior under catalysis.[27,28] In the present work, an interesting result was obtained from the comparison of surface areas and catalytic activities. Despite the different surface areas, nearly similar performances were observed for decomposition reactions of fructose. In other words, there was no relationship between the surface area and activity of the catalysts under sub-CW conditions. Usually two different unique sites of ZrP solids may be responsible for catalytic activities.[28] One of the sites belong to hydroxyl groups (Brønsted sites), while the nature of the second type of site is not clearly understood as of yet, but it is potentially a Lewis acid type. Based on what we obtained from different surface areas and their activities, it can be concluded that surface hydroxyl groups were not solely responsible for the catalytic activities, and the Lewis acid sites could play a relevant role in the catalytic reactions. Another possibility may be attributed to the existence of new phases not previously reported.

Table 2 (G2–3 to L2–3) shows that the calcined samples had no similar influence on the decomposition reaction of fructose. With the increase of calcination temperature, catalytic activity decreased a little. Conversion of fructose decreased about 2–16%, and consequently the selectivity and absolute yield of HMF decreased about 3–16% and 4–20%, respectively. On the other hand, there was a relation between the surface areas of calcined samples and their catalytic activities. For example, the catalyst ZrP (100:600) with a surface area of 6.7 m^2/g rendered about 11% and 6.8% lower yield and selectivity, respectively, than ZrP (0:600) with a surface area of 43.8 m^2/g. If we assume that most of the hydroxyl groups of the surface acids condense at higher temperatures, then again it can be concluded that Lewis acid sites play a major role as the catalytic sites. However, the decreasing yield of the former samples may be attributed to less accessibility of Lewis acid sites for the reaction process (Table 2, G3 and L3). Another possibility is the regeneration of some hydroxyl groups originating from the hydrolysis of P–O–P (condensed) bonds caused by the water at high temperature.[42] However, less activity compared to non-calcined samples may be ascribed to the number of released hydroxyl groups.

Contrary to what was previously reported for the decomposition reaction of fructose under the normal (temperature and pressure) conditions,[43] it was evident that in the presence of the ZrP solid acids, there were not any side-reaction products, including rehydration of HMF to levulinic and formic acids and/or isomerization to glucose. Byproducts identified were limited to soluble polymers and furaldehyde. One of the well-known reaction pathways under the normal conditions for the rehydration reaction is the presence of hydronium-ion species within the macroporous of solid acids,[44] which may catalyze HMF to levulinic and formic acids. From Figures 2 and 3 it was found that the ZrP solids may have only a very small proportion of macroporous structures. Therefore, the non-appearance of any rehydration products (levulinic and formic acid) may be ascribed to the low availability of macroporous structures, which as reported before, have a main role in the dehydration reaction. The decomposition pathways of fructose and byproducts, from another point of view, can be explained by the surface acidity of catalysts and or the acidity of the reaction media. It has already been reported[45] that it is possible to form levulinic and formic acids from the decomposition of fructose at pH <2.7 under the normal reaction conditions, but at pH >3.9, no formation of HMF is observed. It seems that under sub-CW conditions, the catalysts tested showed moderate acidity, so that no rehydration products were identified in the sub-CW decomposition reactions.

In all experiments, the results of total organic carbon analysis did not show formation of any solid polymers (Humin).

3.3. Solid acid catalyst reactions: study of the reaction conditions

From the evaluation of the performances of different ZrP solids, the amorphous form [ZrP (0:0)] was selected for further studies, mainly because of the higher catalytic activity than that of either the semi-crystalline or crystalline ones. A series of experiments were done at a variety of residence times and catalyst-to-substrate ratios (1:1, 1:2, and 1:4) under sub-CW conditions at 240 °C in order to determine better reaction parameters (Table 3). Fructose and glucose, which are an example of a ketohexose and an aldohexose, respectively, were used as substrates. From Table 3 it can be seen that the conversion of substrate and selectivity were controlled by the residence time and the amount of catalyst. As mentioned before, the selectivity of soluble polymers was calculated by difference (Table 3), which was attributed to the lost amounts in decomposition reaction of fructose and glucose.

For both substrates, with increasing residence time up to 240 s with any catalyst-to-substrate ratio, the conversion amount increased. The conversion of glucose was

Table 3. Effect of residence time and catalyst/substrate ratio on dehydration reaction of fructose and glucose under sub-CW conditions at 240 °C, 3.35 MPa and amorphous ZrP [ZrP (0:0)] as acid catalyst

Entry		Substrate	Catalyst/fructose (w/w)	Residence time (s)	Conversion (%)	Selectivity (%) to			Absolute yield of HMF (%)
						HMF	FA[a]	Soluble polymers[b]	
N	1	Fructose 1 wt%	1:1	60	45.1	56.1	1.8	42.1	25.3
	2			120	88.5	56.2	2.8	41.0	49.7
	3			180	96.6	55.4	3.3	41.3	53.5
	4			240	98.6	44.9	3.2	51.9	44.3
O	1		1:2	60	41.7	50.2	2.2	47.6	20.9
	2			120	79.6	61.8	2.3	35.9	49.1
	3			180	94.6	55.7	2.9	41.7	52.8
	4			240	97.5	44.6	3.1	47.7	43.5
P	1		1:4	60	37.1	54.6	1.8	43.6	20.2
	2			120	78.4	56.1	2.2	41.7	44.0
	3			180	94.0	53.4	2.5	44.1	50.2
	4			240	97.0	42.5	2.8	54.7	41.2
Q	1	Glucose 1 wt%	1:1	60	21.2	21.1	0.4	78.4	4.5
	2			120	40.8	34.9	0.8	64.3	14.2
	3			180	53.1	39.0	1.5	59.5	20.7
	4			240	72.3	32.6	1.6	65.8	23.5
R	1		1:2	60	19.3	18.6	0.5	80.9	3.6
	2			120	38.7	31.7	0.7	67.6	12.3
	3			180	48.9	37.4	5.0	62.1	18.3
	4			240	63.9	31.5	1.4	67.1	20.1
S	1		1:4	60	17.3	18.3	0.5	81.2	3.2
	2			120	36.9	32.9	0.7	66.4	12.1
	3			180	46.6	36.4	0.8	62.8	17.0
	4			240	60.9	30.5	1.3	68.2	18.6

[a] Furaldehyde.

[b] Amounts of soluble polymers calculated by difference.

less than that of fructose under identical conditions. This can be attributed to less reactivity of aldohexoses than ketohexoses in the dehydration and/or decomposition reactions. Similar behavior was obtained in the presence of phosphoric acid as catalyst in our previous work.[16] In addition the conversion of the substrate was a function of its ratio with the catalyst.

Usually it is difficult to get higher selectivity of HMF in aqueous reactions due to formation of soluble polymers from polymerization of the substrate and/or HMF, cleavage of HMF to levulinic and formic acid, and other decomposition products. Generally the selectivity of the reaction varies with the reaction media, initial concentration of substrate, reaction temperature, residence time, catalyst type, pH of solution, and other relevant factors. The experimental results showed the best selectivity of nearly 61% from about 80% of conversion of fructose after 120 s residence time and with a catalyst-to-fructose ratio of 1:2 (see Table 3, O2). At longer residence times, the selectivity did not change in spite of increasing the conversion of fructose. It can be concluded that with increasing residence time, in addition to formation of HMF, the formation of polymers as the main side-reaction increased. Therefore, in spite of the increasing conversion of fructose, as shown in Table 3, the selectivity did not increase more than about 61%.

In the case of glucose as substrate, the best selectivity for HMF, about 39%, was obtained from conversion of nearly 53% after 180 s residence time, with a catalyst-to-substrate ratio of 1:1.

For the comparison of two substrates, in the case of glucose, longer residence time and larger amounts of catalyst were necessary to obtain higher selectivity than that of fructose. Table 3 shows that in the case of fructose as substrate, with increasing residence time, the yield of HMF initially increased and then decreased due to polymerization reactions. In the case of glucose, there is a linear increase in the yield of HMF with residence time. Due to lower reactivity of aldohexoses compared to ketohexoses, it seems that even with longer residence times, although soluble polymers are produced, there is still an adequate amount of substrate for the reaction process. Therefore increasing the amount of HMF by residence time can be observed.

Under all conditions the production and/or decomposition amount of furaldehyde was almost similar to that of HMF. And also contrary to what is observed in the dehydration of fructose, the isomerization of glucose to fructose was identified in the dehydration reaction, starting with glucose as substrate.

The turnover frequency (TOF) is usually used for expression of the effect of solid catalysts on the reaction, which contains the parameters of selectivity, conversion, catalyst amount, and residence time (see Eq. 4). In comparison of sub-critical water with conventional methods for dehydration of fructose, based on calculations, a TOF of 26.77 $\text{g g}^{-1}\text{ h}^{-1}$ was obtained for 80% conversion and for best selectivity to HMF under sub-CW conditions (Table 3, O2). This value is much higher than those reported for the conversion of fructose by using ZrP solid acids with classical methods. The maximum TOF reported[28,34] was less than 1.80 $\text{g g}^{-1}\text{ h}^{-1}$. The TOF can be decreased by decreasing selectivity, and increased by shortening the residence time. In sub-CW reactions, because of the short residence time compared to what was already reported for conventional methods (30–60 min), the TOF showed a quite higher value.

3.4. Regeneration of the ZrP solid acids

After using ZrP solid acids in the sub-CW reaction, regeneration is necessary. The results showed that these solids could be regenerated after 30 min shaking in a solution of 2 N of phosphoric acid. After drying, the catalysts can be recycled back to a fresh batch reactor about 6–7 times without losing any catalytic properties such as selectivity and activity. However, after using these 6–7 times, their catalytic properties decrease somewhat. Therefore these results showed an important improvement with respect to the sub-CW reactions using mineral acids.

3.5. Effect of ZrP solid acids on the corrosion of sub-CW reactors

One of the advantages of heterogeneous catalysts is lower corrosion of reactors compared to that experienced with homogeneous acids. For comparison, two series of experiments were done for the dehydration reaction of fructose by using ZrP (0:0) and phosphoric acid[16] at pH 2 as heterogeneous and homogeneous acid catalysts, respectively. The contents of the reactors after reaction at 240 °C for 120 s were analyzed for iron, which may correspond to the amount of corrosion in the reactors. With ZrP, solid acid and iron ions were not identified. However, an iron content of about 10 ppm was detected in the case of phosphoric acid catalyst. In spite of the fact that the sub-CW reactor showed corrosion in the presence of heterogeneous acid catalyst, there was no detected corrosion when using ZrP solid acid.

4. Conclusions

We have found that ZrP solids have catalytic activities under sub-CW conditions for the dehydration of fructose and glucose to HMF. Various kinds of ZrP solids, from amorphous to crystalline forms, were prepared in order to study their catalytic behavior under sub-CW conditions.

The prepared catalysts had no micro and ultra-micro pores. However, very small volumes of macroporous regions were observed. Under sub-CW conditions, no relationship was observed between catalytic activity and the surface area of the catalysts. It seems that not only Brønsted sites, but also Lewis sites of the ZrP solids, are responsible for their catalytic activities. The ZrP solids in amorphous forms were found to have the same or higher activities than the other crystalline forms.

By application of ZrP solids as catalysts under sub-CW conditions, with amorphous forms of the catalyst, about 80% of fructose was decomposed at 240 °C after 120 s, and the selectivity of the dehydration reaction of fructose to HMF rose to 61%. Under the same experimental conditions, starting with glucose as substrate, 39% of selectivity was obtained. The only identified byproducts were soluble polymers and furaldehyde.

These solid acids showed important improvements with respect to using mineral acids. They can be easily separated from reaction media and regenerated and used for several runs. Meanwhile, no corrosion occurred under sub-CW conditions with ZrP solid acids.

Finally, we believe that, based on the type of reactions and substrates, optimization, and modification of these solid acids will increase the performance of catalysts under sub-CW conditions.

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References

1. Fukushima, Y. *R&D Rev. Toyota CRDL* **2000**, *35*, 1–9.
2. Jennings, J. M.; Bryson, T. A.; Gibson, J. M. *Green Chem.* **2000**, *2*, 87–88.
3. Antal, M. J.; Mok, W. S. *Res. Thermochem. Biomass Convers.* **1988**, 464–472.
4. Antal, M. J.; Mok, W. S. *Carbohydr. Res.* **1990**, *199*, 91–109.
5. Bicker, M.; Hirth, J.; Vogel, H. *Green Chem.* **2003**, *5*, 280–284.
6. Fleche, G.; Toulouse, A. G. U. S. Patent 4,339,387, 1982.
7. Seri, K.; Ishida, H. *J. Mol. Catal. A: Chem.* **1996**, *112*, L163–L165.
8. Lewkowski, J. *Arkivoc* **2001**, *2*, 17–54.
9. Kuster, B. F. M.; Der Baan, H. V. *Carbohydr. Res.* **1977**, *54*, 165–176.
10. Harris, D. W.; Feather, M. S. *J. Org. Chem.* **1974**, *39*, 724–725.
11. Moye, C. J.; Goldsck, R. J. *J. Appl. Chem.* **1966**, *16*, 206–208.
12. Szmant, H. H.; Chundury, D. D. *J. Chem. Technol. Biotechnol.* **1981**, *31*, 135–145.
13. Mendnick, M. L. *J. Org. Chem.* **1962**, *27*, 398–403.
14. Chen, J.; Kuster, B. F. M.; Der Wiele, K. V. *Biomass Bioenergy* **1991**, *1*, 217–223.
15. Jow, J.; Rorrer, G. L.; Hawley, M. C. *Biomass* **1987**, *14*, 185–194.
16. Salak Asghari, F.; Yoshida, H. *Ind. Eng. Chem. Res.* **2006**, *45*, 2163–2173.
17. Kuster, B. F. M. *Starch* **1990**, *42*, 314–321.
18. Seri, K.; Inoue, Y.; Ishida, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1145–1150.
19. Garber, J. D.; Jones, R. E. U. S. Patent 3,483,228, 1969.
20. Szmant, H. H.; Chundury, D. D. *J. Chem. Technol. Biotechnol.* **1981**, *31*, 135–145.
21. Mercadier, D.; Rigal, L.; Gaset, A.; Gorrichon, J. P. *J. Chem. Technol. Biotechnol.* **1981**, *31*, 489–496.
22. Nakamura, Y. Jpn. Kokai Tokkyo Koho, Jpn. Pat. 55013243, 1980.
23. Armaroli, T.; Busca, G.; Carlini, C.; Giuttari, M.; Galletti, A. M. R.; Sbeana, G. *J. Mol. Catal. A: Chem.* **2000**, *151*, 233–243.
24. Moreau, G.; Durand, R.; Razigade, S.; Duhamet, J.; Faugeras, P.; Rivalier, P.; Ros, P.; Avignon, G. *Appl. Catal., A* **1996**, *145*, 211–224.
25. Okuhara, T. *Chem. Rev.* **2002**, *102*, 3641–3666.
26. Bogdanov, S. G.; Valiev, E. Z.; Dorofeev, Yu A.; Pirogov, A. N.; Sharygin, L. M.; Moisseev, V. E.; Galkin, V. M. *J. Phys.: Condens. Matter* **1997**, *9*, 4031–4039.
27. Segawa, K.; Nakajima, Y. *J. Catal.* **1986**, *101*, 81–89.
28. Clearfield, A.; Thakur, D. *J. Catal.* **1980**, *65*, 185–194.
29. Thakur, D.; Clearfield, A. *J. Catal.* **1981**, *69*, 230–233.
30. Moffat, J. B. *Catal. Rev. Sci. Eng.* **1978**, *18*, 18–25.
31. Segawa, K.; Ozawa, T. *J. Mol. Catal. A: Chem.* **1999**, *141*, 249–255.
32. Iwamoto, M.; Nomura, Y.; Kagawa, S. *J. Catal.* **1981**, *69*, 234–237.
33. Watanabe, M.; Aizawa, Y.; Iida, T.; Aida, T. M.; Levy, C.; Sue, K.; Inomata, H. *Carbohydr. Res.* **2005**, *340*, 1925–1930.
34. Benvenuti, F.; Carlini, C.; Patrono, P.; Raspolli, G. A. M.; Sbrana, G.; Antonietta, M. M.; Galli, P. *Appl. Catal., A* **2000**, *193*, 147–153.
35. Clearfield, A.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1964**, *26*, 117–129.
36. Clearfield, A.; Thakur, D. *Appl. Catal.* **1986**, *26*, 1–26.
37. Yoshida, H.; Tavakoli, O. *J. Chem. Eng. Jpn.* **2004**, *37*, 253–260.
38. Alberti, G.; Costantino, U.; Millini, R.; Perego, G.; Vivani, R. *J. Solid State Chem.* **1994**, *113*, 289–295.
39. Barton, T. J.; Bull, L. M.; Klempere, W. G.; Loy, D. A. *Chem. Mater.* **1999**, *11*, 2633–2656.
40. Hattori, T.; Ishiguro, A.; Murakami, Y. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1107–1111.
41. Busca, G.; Lorenzelli, V.; Galli, P.; Ginestra, A.; Patrono, P. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 853–864.
42. Ginestra, A. L.; Patrono, P.; Berardelli, M. L.; Galli, P.; Ferragina, C.; Massucci, M. A. *J. Catal.* **1987**, *103*, 346–356.
43. Kuster, B. F. M. *Carbohydr. Res.* **1977**, *54*, 177–183.
44. Moreau, C.; Durand, R.; Pourcheron, C.; Razigade, S. *Ind. Crops Prod.* **1994**, *3*, 85–90.
45. Kuster, B. F. M.; Temmink, H. M. G. *Carbohydr. Res.* **1977**, *54*, 185–191.