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1. Introduction

Furfural is an important heterocyclic compound and organic intermediate. Lots of derivatives which have been widely used in synthetic plastics, pharmaceuticals, pesticides industries could be obtained through hydrogenation, oxidation, and condensation of furfural. The production of furfural is firstly realized by utilizing mineral acids (mainly sulfuric acid) as catalysts from renewable biomass-derived carbohydrates.¹ Chloride salts are often used to increase the furfural production.² The biomass rich in pentosans such as corn cob, sugar cane bagasse, oat hulls could be used to produce furfural. The strong corrosive effect on experiment apparatus, difficult recycle and reuse, serious environmental pollution of sulfuric acid encourage the exploring of novel catalytic processes green to environment as well as with economic properties.

A variety of solid catalysts have been employed in xylose dehydration reaction, *e.g.* zeolites,³⁻¹¹ mesoporous molecular sieve MCM-41,¹² MCM-41-supported niobium-oxide,¹³ heteropolyacids,¹⁴⁻¹⁶ sulfated TiO₂, ZrO₂ and SnO₂,¹⁷⁻¹⁹ modified silicas with porous structure,²⁰⁻²⁴ sulfonated graphene oxide,²⁵ microporous and mesoporous niobium silicates (AM-11),²⁶ microporous silicoaluminophosphates,²⁷ solid acid and base in one-pot,²⁸ ion-exchange resins,^{29,30} exfoliated titanate, niobate and

High performance mesoporous zirconium phosphate for dehydration of xylose to furfural in aqueous-phase

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The conversion of sugars to chemicals in aqueous-phase is especially important for the utilization of biomass. In current work, zirconium phosphate obtained by hydrothermal methods using organic amines as templates has been examined as a solid catalyst for the dehydration reaction of xylose to furfural in aqueous-phase. The use of dodecylamine and hexadecylamine in the synthesis process results in mesoporous zirconium phosphate with uniform pore width of ~2 nm and in morphology of nanoaggregates, which is characterized by powder X-ray diffraction, N₂ isothermal sorption, NH₃ temperature-programmed desorption, FT-IR, and ³¹P MAS NMR spectroscopy. When used as a catalyst for xylose dehydration to furfural in aqueous-phase, the mesoporous zirconium phosphate presents excellent catalytic performance with high conversions up to 96% and high furfural yields up to 52% in a short time of reaction. Moreover, the catalyst is easily regenerated by thermal treatment in air and shows quite stable activity. The open structure with numerous active sites of the Brønsted/Lewis acid sites is responsible for the high catalytic efficiency of mesoporous zirconium phosphate.

titanoniobate nanosheets,³¹ vanadium phosphates,³² and other acidic oxides.33-37 Lewis acid is an efficient catalyst for xylose isomerization to xylulose which is more rapidly dehydrated to furfural on a Brønsted acid.38 It has been reported the furfural selectivity in xylose dehydration is a direct function of the density of Brønsted acid sites.33 Therefore, a suitable ratio between the densities of Brønsted acids and the Lewis acids and the cooperation among them over the solid acid catalysts are much more important to produce furfural in high efficiency. Due to the relative strong Brønsted acidity of hydroxyl groups together with the relative strong Lewis acidity of the metal centers simultaneously, metal phosphates have attracted considerable attention as solid acid catalysts. In an earlier report, zirconium phosphate has a layered structure consisting of zirconium atom planes and planes of phosphate species, and it exhibits both Lewis and Brønsted acidity.³⁹ Zirconium phosphate (ZrP) catalyst has shown interesting performance for xylose conversion to furfural among the solid acid catalysts such as SiO₂-Al₂O₃, WO_x/ZrO₂, γ-Al₂O₃ and HY zeolite.33

In terms of solvent used in the dehydration of xylose, organic and polar solvent such as dimethylsulfoxide (DMSO) or mixed solvent such as water-toluene (W/T) are adopted by many research groups to promote the yield of furfural, due to the timely extraction and separation of the product and the reactant. The decomposition of DMSO at high temperatures in the presence of air and the use of large quantities of toluene, however, would be questions to meet the actual demand. Considering the demands on green routes for the furfural production in the future, water should be the most suitable and

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convenient solvent for the practical utilization of sustainable biomass. Some reports have achieved interesting results in the aqueous media for xylose conversion. The catalysts include TiO₂/CB (carbon black),³⁷ mesoporous (zirconium, aluminium)tungsten,35 and aluminosilicates.9 Considering both Lewis and Brønsted acidity in the zirconium phosphate³⁹ and based on our previous work on morphology controlled synthesis of metal phosphates,⁴⁰ a convenient route to mesoporous zirconium phosphate has been developed in this work. The zirconium phosphate obtained through hydrothermal method with mixed amines as templates at high temperature (180 °C) has large surface area and mesoporous structure. It has offered excellent catalytic performance for dehydration of xylose to furfural in water with high yield of furfural up to 52% in 2 h of reaction at 170 °C. The catalyst is also easily regenerated by thermal treatment and exhibits good performance in reuses.

2. Results and discussion

2.1. Characterization

XRD patterns of a series of prepared zirconium phosphate (ZrP) samples are shown in Fig. 1. The as-prepared ZrP-HT, ZrP-HF can be indexed as $Zr(HPO_4)_2 \cdot H_2O$ (JCPDS PDF no. 34-0127). The two samples present phase transformation after the loss of water in crystal upon heating and the calcined samples, named as ZrP-HT-C, ZrP-HF-C, can be indexed as $Zr_2H(PO_4)_3$ (JCPDS PDF no. 38-0004) and ZrP_2O_7 (JCPDS PDF no. 36-0188), respectively. The ZrP-HT-Am-C, with weak diffraction peaks, could be rather defined as amorphous. The BET (Brunauer-Emmett-Teller) specific surface areas and pore volumes obtained by the nitrogen physisorption are presented in Table 1. As shown in Fig. 2a, the sorption isotherm of ZrP-HT-Am-C presents a significant hysteresis loop at $p/p_0 > 0.45$ with type IV



Fig. 1 XRD patterns of prepared zirconium phosphates. (ZrP-HT: zirconium phosphate synthesized without amines; ZrP-HT-C: ZrP-HT calcined; ZrP-HF: zirconium phosphate synthesized with HF; ZrP-HF-C: ZrP-HF calcined; ZrP-HT-Am-C: zirconium phosphate as synthesized with organic amine after calcination).

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Table 1 Structural and surface properties of the zirconium phosphate samples

Sample	${S_{\mathrm{BET}}}^a (\mathrm{m}^2 \mathrm{g}^{-1})$	$V_{\rm p}^{\ b} \ ({\rm cm}^3 {\rm \ g}^{-1})$	Brønsted acid ^{c} (µmol g ⁻¹)	Lewis acid ^{c} (μ mol g ⁻¹)	
7rD_HE_C	o	0.02			
ZrP-HT-C	20	0.02	_	_	
ZrP-HT-Am-C	316	0.55	229	307	
$H_{3}PO_{4}$ (1.3%)	_	_	_	—	

 a BET specific surface area. b Pore volume calculated from N_2 adsorption at $p/p_0 \sim 0.97.$ c Calculated based on published extinction coefficients for the bands at 1545 and 1454 $\rm cm^{-1}.^{41}$

isotherm, indicative of typical mesoporosity upon the addition of organic amines in the preparation. Both ZrP-HT-C and ZrP-HF-C show low BET specific surface area (20 and 8 m² g⁻¹, respectively), but the ZrP-HT-Am-C sample exhibits much higher surface area (316 m² g⁻¹). The pore size distributions shown in Fig. 2b reveals a broad one in ZrP-HF-C and a relatively narrow one centered at 6 nm in ZrP-HT-C. A narrow pore size distribution centered at 2 nm is observed in ZrP-HT-Am-C with much larger pore volume.

SEM images of ZrP-HT-C and ZrP-HF-C, shown in Fig. 3A and B, reveal the samples as general exfoliation of layered materials without the existence of mesopores, in agreement with their low surface area. The TEM images of ZrP-HT-Am-C, depicted in Fig. 3C and D, indicate the sample consisting of small particles connected each other with rich mesoporous structure to resulting in high surface area as measured by nitrogen sorption.

The FT-IR spectra of the samples are shown in Fig. 4. For the ZrP-HT-Am sample, the peak of 1626 cm⁻¹ is attributed to bending vibrations of water molecules, while the bands in the region 1000–1200 cm⁻¹ are due to $-PO_4$ stretching vibrations. The bands at 2921 and 2846 cm⁻¹ are attributed to stretching vibrations of $-CH_2$ in the organic amines. The bands at 1464 and 720 cm⁻¹ are from the distorted vibration absorptions of $-CH_2$. The IR spectrum of ZrP-HT-Am-C after calcination shows a relatively simple structure along with disappearances of characteristic peaks of $-CH_2$. For ZrP-HT and ZrP-HF, the peaks of 3590, 3507 and 3135 cm⁻¹ correspond to the symmetric and asymmetric stretching vibrations of lattice water, respectively.⁴² The peak of 1615 cm⁻¹ is attributed to bending vibrations of water molecules. The absorbance at 1247 cm⁻¹ is usually attributed to a hydrogen phosphate characteristic peak. Also the



Fig. 2 (a) N_2 physisorption isotherms at $-196\ ^\circ C$ and (b) pore size distribution curves of the samples.

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Fig. 3 FESEM images of (A) ZrP-HT-C and (B) ZrP-HF-C. (C) and (D) TEM images of ZrP-HT-Am-C (inset shows the magnified part as pointed).



Fig. 4 FT-IR spectra of samples before and after calcination.

set of peaks in range of 1000–1200 cm^{-1} are belonged to $-\text{PO}_4$ stretching vibrations.

The NH₃-TPD results are shown in Fig. 5a. A broad desorption peak appeared around 120 $^{\circ}$ C for all three samples is attributed to desorption of NH₃ weakly bound to the surface of the zirconium phosphate samples. Only small amount of desorbed ammonia is detected from ZrP-HF-C and ZrP-HT-C sample due to their low density of acid sites. For ZrP-HT-Am-C, a desorption peak centered at ~260 $^{\circ}$ C, besides the peak around 120 $^{\circ}$ C, is also observed, indicative of the ammonia adsorbed on



Fig. 5 (a) NH₃-TPD profiles and (b) pyridien-IR spectra of ZrP-HF-C, ZrP-HT-C and ZrP-HT-Am-C samples.

the P–OH groups and/or some strong Lewis acid sites. The desorption of the ammonia at high temperature is absent in the other two samples ZrP-HF-C and ZrP-HT-C, implying the lack of large quantity of strong acid sites in these two samples. The IR spectrum of chemically adsorbed pyridine on mesoporous ZrP-HT-Am-C sample reveals the coexistence of Lewis and Brønsted acid sites, by bands of absorption at 1454 cm⁻¹ and 1545 cm⁻¹, as shown in Fig. 5b. The quantitative results on density of Brønsted and Lewis acid sites are obtained from the pyridine adsorption IR spectrum and listed in Table 1. In contrast, no obvious absorption of the adsorbed pyridine is detected from the IR spectra on both ZrP-HF-C and ZrP-HF-C samples after evacuation at 150 °C (Fig. 5b).

2.2. Xylose dehydration

Scheme 1 shows the reaction of xylose dehydration to furfural. Considering the demand on green processes, the xylose



Scheme 1 The dehydration reaction of xylose to furfural.



Fig. 6 Conversion of xylose and yield of furfural in the presence of different catalysts. *Reaction conditions*: xylose (0.4 g), catalyst (0.1 g), water (40 mL), 140 °C, 2 h.

dehydration is performed in an aqueous system and the primary results of reaction at 140 °C with reaction time of 2 h are summarized in Fig. 6. In a blank test, 13% conversion of xylose and low selectivity of ~13% to furfural are detected due to the action of high temperature water. For the catalysts of ZrP-HF, ZrP-HT, ZrP-HF-C and ZrP-HT-C, the selectivity to furfural is significantly improved, but the conversion of xylose is still very low (<12%). The as-prepared ZrP-HT-Am with presence of amines shows improved conversion (20%) and selectivity (34%). After calcination, ZrP-HT-Am-C exhibits inspiring catalytic performance with 52% conversion and 50% selectivity. For comparison, the catalytic reaction in the presence of liquid acid

of H_3PO_4 (1.3 wt%, equal to the amount of P species in the ZrP-HT-Am-C used) is also performed, in which 33% of furfural selectivity and 14% of xylose conversion are detected. For the dehydration of xylose to furfural, it has been reported that the xylose isomerizes to xylulose on a Lewis acid and then the xylulose dehydrates to furfural on a Brønsted acid.³⁸ According to the structure of the current ZrP-HT-Am-C, it is neither a strongly acidic material nor a strongly basic material but possesses large number of Lewis acid and Brønsted acid simultaneously. Its good performance for the conversion reaction of xylose would be assigned to the effective cooperation between the Lewis and Brønsted acid sites.

The effect of xylose/catalyst ratio on the xylose dehydration reaction is investigated with ZrP-HT-Am-C as catalyst and the results are shown in Fig. 7a. The conversion of xylose monotonically increases with the catalyst amount. But the best selectivity to furfural is observed at the ratio of xylose/catalyst around 4. With the increase in reaction temperature, as shown in Fig. 7b, the xylose conversion increases monotonically and the selectivity to furfural basically keeps at constant in the range of 140-170 °C. At 170 °C, 96% conversion and 52% yield to furfural are measured. It is very interesting that the selectivity to furfural over the ZrP-HT-Am-C is almost constant versus the conversion of xylose (Fig. 7c), implying the continuous reaction of furfural on the ZrP-HT-Am-C catalyst could not happen. This should be very important phenomenon offering a research clew for the future development of new catalyst based on zirconium phosphate.

The reaction results of current work are summarized in Table 2, and some results of xylose conversion to furfural with water as solvent reported in literature are also listed. The performance of current ZrP-HT-Am-C is amongst high performance catalysts documented. Considering the catalyst concentration used in batch reactor, the present catalyst ZrP-HT-Am-C with load of 2.5 $g_{cat} L^{-1}$ gives fairly high conversion of xylose and selectivity to furfural at the same time in aqueous-phase reaction. The solvent effect on the furfural production from the xylose dehydration over ZrP-HT-Am-C is



Fig. 7 (a) Effect of amount of ZrP-HT-Am-C on furfural production from the xylose dehydration reaction. Xylose: 0.4 g, water: 40 mL, temp.: 140 °C, reaction time: 2 h. (b) Variation of catalytic performance with temperature over ZrP-HT-Am-C. Xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, reaction time: 2 h. (c) Furfural selectivity *versus* xylose conversion at 140–180 °C in aqueous reaction for 2 h. \blacksquare xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 100 °C; \blacklozenge xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 120 °C; + xylose 0.4 g, cat.: 0.1 g, water: 40 mL, 140 °C; \bigcirc xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 140 °C; \bigcirc xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 140 °C; \bigcirc xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 140 °C; \bigcirc xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 140 °C; \bigcirc xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 140 °C; \bigcirc xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 140 °C; \bigcirc xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, reuse after 2 h reaction at 140 °C; \bigcirc second regeneration by calcination at 500 °C in air after 2 h reaction at 140 °C; \bigcirc second regeneration by calcination at 500 °C in air after 2 h reaction at 140 °C; \bigcirc xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40 mL, 160 °C; \diamondsuit xylose: 0.4 g, cat.: 0.1 g, water: 40

Table 2 Performance of different catalysts in the dehydration of the xylose to furfural in a water system^a

Catalysts	Solvent	$T(^{\circ}C)$	Time (h)	Xylose conv. (%)	Furfural yield (%)	Xylose/catalyst	Catalyst $(g_{cat} L^{-1})$	Ref.
ZrP-HT-Am-C	DMSO	140	2	60	15	4	2.5	This work
ZrP-HT-Am-C	H ₂ O/toulene ^b	140	2	16	12	4	2.5	This work
ZrP-HT-Am-C	H_2O	140	2	52	26	4	2.5	This work
ZrP-HT-Am-C	H_2O	170	2	96	52	4	2.5	This work
TiO ₂ /CB	H_2O	170	2.5	94	47	3	10	37
Zr(W,Al) mixed oxides	H_2O	170	8	93	47	1.5	20	35
H-MCM-22, ITQ-2	H_2O	170	32	91-97	54-56	1.5	20	9
MSHS	H_2O	170	1	32	18	9	3.3	21
VPO	H_2O	170	4	80	24	1.5	20	32

also tested, as shown in Table 2. In general, for current catalyst

ZrP-HT-Am-C, both the DMSO and mixed H_2O -toluene systems give inferior performance for the reaction, indicating the zirconium phosphate material prepared in present work is an effective catalyst for xylose dehydration to furfural in the water system.

The reusability of the ZrP-HT-Am-C catalyst is tested with the catalyst separated by filtration from the reaction suspension. The catalyst filtrated for reuse is thermally treated in air at 500 °C for 4 h before the next run. The results are shown in Fig. 8 and it can be concluded that the thermal treatment between reuse intervals basically regenerates the catalyst performance. The catalyst shows fairly good property and stability for the reaction of xylose dehydration to furfural. Simultaneously, only trace amount of zirconium is detected by ICP analysis in the solution with catalyst separated after reaction. The variation of the catalytic property of ZrP-HT-Am-C with the reaction time is also tested and the results are shown in Fig. 9. At 170 °C, the conversion of xylose reaches 96% in 2 h of reaction with 52% selectivity to furfural. In prolonged time of reaction, the slight decrease in the selectivity to furfural indicates the minor transformation of furfural to by-products, implying the fairly good stability of furfural under the reaction conditions.



Fig. 8 Reuse study for the ZrP-HT-Am-C catalyst at 170 °C after 2 h reaction. *Reaction conditions*: xylose (0.4 g), catalyst (0.1 g), H_2O (40 mL). For the second and third run, the catalyst is regenerated at 500 °C for 4 h in air.



Fig. 9 The catalytic performance of ZrP-HT-Am-C sample upon the reaction time at 170 $^\circ\text{C}.$

The excellent performance of ZrP-HT-Am-C catalyst should be ascribed to its open mesoporous structure with numerous and accessible active sites. The Zr/P ratio in the sample was determined as 0.8 by XRF analysis. And the state of phosphorus species in ZrP-HT-Am-C is detected by solid sate ³¹P MAS NMR spectroscopy. The spectrum is presented in Fig. 10. The broad line between -15 and 35 ppm is attributed to the P species neighboring to Zr species. There are no signals of pyrophosphates which appeared in the range of -35 to -45 ppm.⁴³ Subtle acid structure in this special materials, such as the quantity and relative position of the Brønsted and Lewis acid sites, is



Fig. 10 Solid state ³¹P MAS NMR spectrum of ZrP-HT-Am-C.

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responsible for its excellent performance for the reaction. The delicate cooperation among the Brønsted and Lewis acid sites is full of charm of research, which causes the adsorbed xylose transformed effectively and selectively. Related investigation using NMR method with designed probe molecules is under way in our lab. The current results are important for the future research on the conversion of sugars to useful chemicals.

3. Experimental

3.1. Catalyst preparation

The zirconium phosphate was synthesized by hydrothermal method.40 In a typical synthesis, 24 mL of ethanol solution containing 4.0 g dodecylamine (J & K Technology Co., Ltd.) and 0.50 g hexadecylamine (J & K Technology Co., Ltd.) was pumped slowly (0.25 mL min⁻¹) into 80 mL of aqueous solution containing zirconium nitrate pentahydrate (Sinopharm Chemical Reagent Co. Ltd, 3.0 g) and ammonium dihydrogen-phosphate (Nanjing Chemical Reagent Co., Ltd., 1.03 g) at 40 °C. The mixture was transferred into a Teflon-lined autoclave and sealed before hydrothermally heating in an oven at 180 °C for 8 h, and then cooled down and centrifuged to obtain the solid product. The solid was further washed by water and anhydrous ethanol repeatedly and dried under vacuum at 60 °C for 24 h. The resulted sample was further subjected to calcination at 500 °C for 4 h in an air atmosphere. The samples before and after calcination treatment were noted as ZrP-HT-Am and ZrP-HT-Am-C, respectively.

The other zirconium phosphate using hydrothermal method without organic amine was prepared as follows. Zirconium oxychloride octahydrate (Sinopharm Chemical Reagent Co., Ltd, 0.68 g) was dissolved in 25 mL water at room temperature, the concentrated phosphoric acid (1 mL) was dropwise into the zirconium oxychloride aqueous solution at continuous stirring. Then the mixture was transferred to the sealed Teflon-lined autoclave and put into an oven at 180 °C for 6 h. After hydrothermal treatment, the mixture was cooled down, centrifuged and washed. The resulted product was dried under vacuum at 60 °C for 24 h and then subjected to the oven at 500 °C for 4 h in air. The samples before and after calcination treatment were marked as ZrP-HT and ZrP-HT-C, respectively.

The zirconium phosphate sample using hydrofluoric acid (HF) method was obtained according to the synthesis procedure by Alberti.⁴⁴ Simply, a certain amount of zirconium oxychloride octahydrate, concentrated phosphoric acid, hydrochloric acid and hydrofluoric acid were mixed uniformly in a baker under continuous stirring at room temperature for 96 h. The white precipitate was then centrifuged and washed. The drying and calcination process were the same with the two samples above. The samples were named as ZrP-HF and ZrP-HF-C, respectively.

3.2. Catalyst characterization

XRD patterns of samples were recorded in the 2θ region of 5°– 90° using a diffractometer (Philips X'pert-Pro) with Cu*K* α radiation ($\lambda = 1.5418$ Å). The identification of crystalline phases was made by matching the patters with the JCPDS files. The specific surface areas and pore volumes of samples were obtained by means of nitrogen adsorption measurements at -196 °C using an automated gas adsorption analyzer (Micromeritics ASAP 3020). Samples were pretreated at 300 °C for 2 h under vacuum. Total surface area was calculated using the classical BET (Brunauer–Emmett–Teller) method and the pore volume was evaluated with the *t*-plot method using the equation of Harkins and Jura.

Field emission scanning electron microscopy (FESEM) analysis was carried out on a Hitachi-S4800. Transmission electron microscopy (TEM) images were taken with a JEM-2100 using an accelerating voltage of 200 kV. FT-IR spectra of the prepared zirconium phosphates were recorded on Nicolet iS10 spectrometer using ATR accessory with a resolution of 4 cm⁻¹ and accumulation of 64 scans.

Ammonia temperature-programmed desorption (NH₃-TPD) was carried out in a PX200 apparatus (Tianjin Golden Eagle Technology Limited Corporation). Prior to the measurements, the sample (0.1 g) charged into the quartz U-tube was firstly treated in a He stream at 500 °C for 1 h at a rate of 10 °C min⁻¹. Then the temperature was decreased to 50 °C and NH₃ was switched into the system under a flow of He (40 mL min⁻¹) for 0.5 h adsorption. The desorption of ammonia was performed from 50 °C to 500 °C at a rate of 10 °C min⁻¹. The desorbed NH₃ was detected using a thermal conductivity detector (TCD).

In terms of pyridine IR, the sample was pressed into selfsupporting wafer and activated at 200 °C for 1 h in vacuum (pressure < 10^{-3} mbar). After cooling to room temperature, a spectrum was recorded. Pyridine (1 mbar) was then adsorbed at 150 °C for 0.5 h. After outgassing for 0.5 h to remove physisorbed pyridine, a spectrum was recorded using the spectrum of activated wafer as a background.

Solid-state ³¹P MAS NMR measurement was performed on a 9.4 T Bruker Avance spectrometer at a resonance frequency of 161.97 MHz. Powdered sample was spun at 14 kHz in a 4 mm rotor under ambient temperature. Spectrum was acquired using a single pulse excitation pulse sequence (zg) with a 2.5 μ s pulse length and 600 s recycle delay. ³¹P chemical shifts were referenced to external ammonium dihydrogen phosphate (0.81 ppm).

3.3. Catalysis tests

The batch catalytic experiments were performed in the Amar autoclave (total volume, 100 mL). Typically, xylose (0.4 g), powdered catalyst (0.05–0.3 g) and H_2O (40 mL) were poured into the autoclave, and then the reaction mixtures were heated to the target temperature under continuous stirring at 500 rpm. The mixture after the reaction was cooled with recycled water at once. Xylose conversion and furfural selectivity are calculated using the formula as follows:

$$Conversion\% = \frac{N'}{N_0} \times 100$$
 (1)

 N_0 : moles of xylose initially added to the autoclave. N': moles of xylose consumed.

Selectivity% =
$$\frac{N_1}{N'} \times 100$$
 (2)

 $N_1\!\!:$ moles of fur fural formed during the reaction.

The products were quantitatively determined by Agilent HPLC 1260 equipped with an ion-exchange column (Bio-Rad Aminex HPX-87H column 300 mm \times 7.8 µm), coupled to a differential refractive index detector (for xylose) and an Agilent 1260 UV detector (280 nm, for furfural). A 5 mmol L⁻¹ H₂SO₄ aqueous solution was used as the mobile phase at a flow rate of 0.6 mL min⁻¹ and the column temperature was kept at 65 °C. Pure chemicals, *i.e.* p-xylose and furfural were used for calibration without further treatment.

4. Conclusions

Mesostructural zirconium phosphate is demonstrated to be an effective catalyst for xylose dehydration to furfural in aqueous media. By using dodecylamine and hexadecylamine as templates in the hydrothermal synthesis process, the obtained zirconium phosphate after calcination is poor crystallized but similar to zirconium oxide phosphate and possesses high surface area and rich mesoporosity. For xylose conversion in aqueous media, a furfural yield up to 52% has been achieved at 170 °C for 2 h reaction. The adequate Lewis/Brønsted acid sites which responsible for the isomerization and dehydration in the catalyst would be responsible for its excellent performance of catalysis. In addition, the reuse property of the catalyst seems fairly good by calcination in air at the reuse intervals. The result is important for the future research on the conversion of sugars to useful chemicals.

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