

View Article Online View Journal

RSC Advances

This article can be cited before page numbers have been issued, to do this please use: L. Wang, F. Yuan, X. Niu, C. Kang, P. Li, Z. Li and Y. Zhu, *RSC Adv.*, 2016, DOI: 10.1039/C6RA02602H.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/advances

Effect of Cerous Phosphates with Different Crystal Structures on Their Acidity and Catalytic Activity for Dehydration of Glucose into 5-(hydroxymethyl)furfural

Lina Wang, Fulong Yuan, Xiaoyu Niu, Chuanhong Kang, Pengying Li, Zhibin Li*, Yujun Zhu*

Key Laboratory of Functional Inorganic Material Chemistry (Heilongjiang University), Ministry of Education, School of Chemistry and Materials, Heilongjiang University, Harbin, 150080 P. R. China

* Corresponding Author: Yujun Zhu, Email: yujunzhu@hlju.edu.cn, Zhibin Li, Email: lizb@hlju.edu.cn, Tel: +86-451-86609650; Fax: +86-451-86609650

Abstract

A series of Cerous phosphates (CP) catalysts with different crystal structures were synthesized by hydrothermal method at different temperature (120, 140, 160, 180 and 200 °C) and their performance for the dehydration of glucose into 5-(hydroxymethyl)furfural (HMF) were also well investigated. These catalysts were characterized by XRD, N₂ adsorption-desorption, SEM, In-situ DRIFT, NH₃-TPD and XPS. The results indicate the change of the synthesized temperature will lead to the transformation of crystal phase and morphology from 120 °C (nanoparticles, hexagonal structure) to 200 °C (nanorods, monoclinic structure), and different crystal phases possess different surface Ce⁴⁺ amount and acidity. A well linear correlation is found between Lewis acid contents and the surface Ce⁴⁺ amount among these CP catalysts, and a very well linearity is also displayed between Lewis acid amount and conversion of glucose or selectivity of HMF, which indicates Lewis acid plays an important role in the dehydration of glucose to HMF. CP120 with hexagonal crystal

structure exhibits the best catalytic activity (conversion 97% of glucose and yield 61% of HMF) due to the maximum amount of Lewis acid and total acid.

Keywords: Cerous Phosphates; Ce⁴⁺ Lewis acid; hexagonal structure; dehydration of glucose;

5-(hydroxymethyl)fulural

Introduction

Published on 07 April 2016. Downloaded by Université Laval on 08/04/2016 08:10:16.

As the decline of fossil resource and the concern of CO₂ emission, the utilization of renewable sources such as solar, nuclear, wind energy and biomass resource, have attached extensive interests.¹⁻⁴ Biomass consist of cellulose, lignose, starch, glucose and fructose have been wildly studied due to the advantage of wide distribution, huge production, renewable, non-pollution^{5,6} and prospective application values.^{7,8} 5-(hydroxymethyl)furfural (HMF), as a sort of green platform molecule derived from biomass, is recognized as a feedstock for the production of advanced chemicals and has been applied in numerous industrial processes. For instance, 2,5-Dimethylfuran from catalytic hydrogenation of 5-HMF, can be used as the additives of automotive liquid biofuel, 2,5-Furandicarboxylic acid from oxidation of 5-HMF was also considered an important valuable chemical as the substitution of terephthalic acid.⁹

Presently, HMF was mainly produced from the catalytic dehydration of fructose and glucose.^{1-5,10,11} High HMF yield transformation of fructose has been reported under aqueous phase, organic solvents phase and water/organic mixture phase.^{2,10} Unfortunately, the transformation of fructose was not suitable for large industrial application due to its high cost even with superior yield of HMF.^{12,13} Glucose offered another alternation as its low cost and easy obtaining, in which glucose firstly was converted to fructose through a isomerization process,^{11,14} then followed conversion to HMF by the dehydration process (Scheme 1).¹⁵

RSC Advances

Many attempts have been applied to find better catalysts for this reaction,¹⁶ for example $H_2SO_4^{11}$, HCl^{17} , metallic oxide¹⁴ and chromium chloride¹⁸ were employed, however, inorganic liquid acid catalysts (H_2SO_4 and HCl) leaded to the increase of humins formed from direct dehydration of glucose and lower selectivity to HMF.^{11,17} In recent years, solid acid catalysts have been applied in catalytic transformation of glucose to HMF. In a study by Zhang and co-workers, amorphous catalysts of Cr_2O_3 , SnO_2 , SrO and grapheme oxide-ferric oxide were used to convert glucose into HMF, however, the metal oxide catalysts fully lost the catalytic activities after calcinations.¹⁴ Zhang et al. also reported the conversion of glucose to HMF over hydroxyapatite supported chromium chloride, but the yield was below 40%.¹⁸ Another study by Jadhav et al. focused on application of zeolite in ionic liquid for producing HMF from D-glucose, but the ionic liquids they used were harmful and expensive.¹⁹

Therefore, designing a high yield and low cost catalyst was considered as a much more important aspect in the conversion of glucose to HMF. Reported work by Ronen et al. studied the formation of fructose via isomerization mainly from Lewis sites and HMF from both Brønsted and Lewis sites.²⁰ Alam and co-workers reported titanium hydrogenphosphate (TiHP) material consisting of both Brønsted and Lewis acid sites, they proposed Brønsted acid sites could accelerate the produce of furan ring opening product when the temperature turned much higher.²¹ Therefore, a catalyst with combination of both Lewis acid (for isomerization) and the subsequent Brønsted acid (for dehydration configuration) may be more prospectively for glucose dehydration to HMF.²¹⁻²⁴

The newly metal phosphates^{20,25-27} were proposed in this reaction, in which metal could provide Lewis acid sites and Brønsted acid sites could obtain from geminal P(OH) groups

RSC Advances

possibly.²⁸ A series of metal Zr/Sn(IV) phosphate catalysts with modified surface acid distribution were synthesized, which exhibited improved catalytic performance due to higher amounts of polyphosphate species.²⁰ Another cerium(IV) phosphates in this reaction were also reported but showed a lower yield (23%–24%) and high stable performance even after several cycles' reaction.²⁷ As the perspective of cerium phosphate species in the glucose to HMF, much more work still need to do to improve their application.

In the present work, a series of CePO₄ catalysts with different crystalline types have been synthesized by a convenient hydrothermal method at different temperatures and their activity have been carried out for dehydration of glucose to HMF. The relationships about total acid amount, Brønsted and Lewis acids to yield and conversion have also been studied. Meanwhile, various reaction conditions, such as reaction temperature, time, loading of catalyst, amount of reaction medium and reusability have also been evaluated to find an optimal reaction conditions for the HMF production.

Experimental

Published on 07 April 2016. Downloaded by Université Laval on 08/04/2016 08:10:16.

Catalysts preparation

CePO₄ (CP) catalysts were prepared by a hydrothermal method. In a typical experiment, Ce(NO₃)₃ (716 mg) and NaH₂PO₄ (869 mg) with mole ratio of 1:1 were dissolved in 20 ml diluted water, respectively, and mixed these two solutions and stirred for 1.5 h, and then transferred into a Teflon reactor with stainless autoclave. The above stainless autoclave was heated at different temperatures (120, 140, 160, 180 and 200 °C) for 8 h in the oven, then cooled to room temperature. The resulting solid was filtered and washed with diluted water for several times, following dried at 100 °C for 12 h. The obtained catalysts were denoted as

CP120, CP140, CP160, CP180 and CP200 according to the hydrothermal temperature.

Characterization of catalysts

X-ray diffraction (XRD) patterns of catalysts were evaluated using a D/max-IIIB diffractometer with a Cuk α radiation (λ =1.5418 Å) combined with a Ni-filter. The morphology of the CP catalysts was investigated by Scanning Electron Microscopy (SEM) (Hitachi S-4800) with an electron gun working at an accelerating voltage of 5 kV. The textural parameters were evaluated from the N₂ physisorption using Micromeritics Tristar II analyzer at -196 °C. X-ray photoelectron spectra (XPS) were performed on a Kratos-AXIS ULTRA DLD with an Al K α radiation source. Binding energies (BE) were referenced to the C (1s) binding energy of carbon taken to be 284.7 eV.

Temperature-programmed desorption of ammonia (NH₃-TPD) was carried out in a full automatic adsorption instrument (XQ TP-5080, China) with a thermal conductibility detector (TCD) and performed in the following procedure. A fixed catalyst bed with 100 mg sample was enclosed in a quartz tube and fixed by two balls of quartz-wool. Firstly, the sample was heated from room temperature to 100 °C with a heating rate of 10 °C/min under He flow (30 ml/min), and then maintained at this temperature for 60 min. the sample was cooled to room temperature, switched to NH₃ flow (30 ml/min) for 1 h. Finally, the sample was heated to 700 °C with a rate of 10 °C/min under He flow (30 ml/min).

In situ DRIFTS experiments were performed on a Nicolet 6700 spectrometer with in situ diffuse reflectance pool and high sensitivity MCT detector which cooled by liquid N_2 . The catalyst was loaded in the Harrick IR cell and heated to 100 °C under N_2 flow (40 ml/min) for 60 min to remove adsorbed impurities, and then cooled to room temperature. The background

RSC Advances

spectrum was collected under a N_2 atmosphere and was subtracted from the sample spectra. When the adsorption of NH₃ on the sample was investigated, the spectra were recorded with N_2 background. The DRIFTS spectra were recorded by accumulating 32 scans with a resolution of 4 cm⁻¹. The total flow rate of the feeding gas was kept 40 mL/min (20 ml/min N_2 , 20 ml/min NH₃).

Catalytic activity measurement

The dehydration reaction of glucose was performed with 50 mg catalyst, 50-250 mg glucose and 5-25 ml dimethylsulfoxide (DMSO) in a 100 ml three-necked flask coated with oil bath at 130-170 °C for 15-150 min under N₂ atmosphere and stirring condition. After the reaction, the mixture was cooled and centrifuged. The obtained liquid was analyzed by high performance liquid chromatography (HPLC). The quantitative analysis of glucose was monitored using HPLC (Shimadzu 20A) equipped with a refractive index detector and a Bio-Rad Aminex HPX-87H column. 5-HMF was analyzed using HPLC (DIONEX Ultimate 3000) with an InterSustain C18 column and a 284 nm UV detector.

Results and discussion

XRD characterization

Published on 07 April 2016. Downloaded by Université Laval on 08/04/2016 08:10:16.

Fig. 1 showed the XRD patterns of the CP catalysts synthesized at different hydrothermal temperatures. For CP120, the diffraction peaks at 2θ of 14.3, 20.0, 25.4, 29.1, 31.4, 37.5, 41.9, 48.2, 53.3 ° were ascribed to the hexagonal crystalline structure of CePO₄ in Fig. 1A, which match well with the standard data of JCPDS 34-1380. However, with the increase in synthesis temperature, the intensity of peaks at 14.3 and 20.0 ° indexed to (100) and (101) crystal plane of CePO₄ with hexagonal structure²⁹, respectively, gradually reduced and the former one

RSC Advances

diminished in CP160, then these two peaks generally disappeared in CP180 and entirely vanished in CP200. Meanwhile, the new peaks at 17.1, 18.9, 21.3 27.0, 34.4 and 41.1° were observed in CP160 (Fig. 1C), which were attributed to (101) (011) (111) (200) (202) and (103) planes of CePO₄ with monoclinic crystalline phase (JCPDS 32-0199), respectively. This crystalline phase dominated fully in CP200 sample.³⁰ This means the crystal phase has been transformed to an utterly monoclinic crystal phase for CP200 sample. It was interesting to note that CP120 exhibited a hexagonal structure and CP200 presented the monoclinic phase, while CP160, CP180 and CP200 demonstrated a mixture structure of these two crystal phase. It reveals the change of hydrothermal temperature can lead to transformation of different crystal phases.

N₂ adsorption-desorption measurement

The textural properties of the CP catalysts derived from the nitrogen physisorption are described in Fig. 2a and summarized in Table 1, the pore distributions are also displayed in Fig. 2b. It can be seen that the CP catalysts exhibited type IV isotherms with a H3 hysteresis loop at $0.4 < p/p_0 < 0.9$ according to the IUPAC classification,³¹ which mean the formation of intercrystal mesopores associated with aggregates of particles in the CP samples.^{32,33} It was also noteworthy that pore volumes decreased from 0.39 cm³/g to 0.26 cm³/g (Table 1, Fig. 2). From Fig. 2b, the pore diameter of CP120 was about 25 nm (Fig. 2b-A), pore diameter turned gradually wider with the increase in hydrothermal temperature, in which the value of that was more than 46 nm, along with a new pore diameter of 101 nm in the CP200. In addition, the BET surface area was 108, 88, 82, 65 and 54 m²/g for CP120, CP140, CP160, CP180 and CP200, respectively (Table 1), which reduces with the increase in the synthesis temperature. It

results from the change of crystal phase from hexagonal structure to monoclinic phase (Fig. 1).

SEM images

The morphology of the CP catalysts was characterized by SEM and shown in Fig. 3. It can be seen easily that CP120 displayed a moderate aggregation and partial accumulation of mesosphere structure with particles dimension at 30-60 nm. CP200 denoted obvious nanorod morphology with the length of 100-300 nm and diameter of 50 nm, while the nanorods formed more cumulated pore structure than that of CP120. For CP160, mixture morphology of relative irregular nanosphere and nanorod was observed. As the variation of synthesis temperature, the morphology of the CP catalysts gradually converted from nanosphere (CP120) to nanorod shape (CP200), and others exhibited the irregular morphology due to their mixture of hexagonal and monoclinic crystalline phases.

NH₃-TPD measurement

The acidity of the CP catalysts was measured through NH₃-TPD as the result shown in Fig. 4. CP120 and CP140 catalysts exhibited a serials of desorption peaks in range of 50-350 °C, which were attributed to the weak NH₃ adsorption.²³ These peaks demonstrate that there are various surface weak acid sites in CP120 and CP140. It was noteworthy that a small NH₃ desorption peak around 450 °C can be observed for CP140, which was assigned to the strong acid sites.²³ While the desorption peaks around 50-350 °C became very weak for CP160, CP180 and CP200, to the contrary, the peak at about 500 °C attributed to the strong acid sites strengthened. The total amount of the acid sites were calculated by NH₃-TPD which was 1.67, 1.39, 1.29, 1.21 and 0.79 mmol/g for CP120, CP140, CP160, CP180 and CP200, respectively.

It demonstrates that the total acid amount decreases with increasing the hydrothermal temperature, and CP120 possesses the most total acid amount assigned to weak acidity sites among all these catalysts. These results can be attributed to the full transformation from hexagonal to monoclinic phases. Consequently, it is suggested that CP catalyst with monoclinic crystalline phase may provide strong acid site, while in another aspect, weak acid is mainly formed in hexagonal crystalline structure.

NH₃-DRIFT measurement

As we know, Brønsted and Lewis acid sites can not be distinguished clearly by NH₃-TPD measurement. Thus, DRIFT spectra of NH₃ absorbed on the surface acid site of the CP catalysts were performed in order to obtain the amount of Brønsted and Lewis acid. Fig. 5 shows the IR spectra of the CP catalysts after NH₃ adsorption. The strong band at 1690 cm⁻¹ was observed for the CP catalysts, which was assigned to the NH4⁺ bending vibration on Brønsted acid site,^{34,35} elsewhere, two weaker ones at 1221 and 1578 cm⁻¹ were detected which were attributed to the asymmetric and symmetric bending vibrations of coordinated NH₃ on Lewis acid site.³⁶⁻³⁸ Combined the total acid amount form NH₃-TPD (Table 1), the amount of Brønsted and Lewis acid can be calculated according to the peak area ratio of Brønsted acid site (1690 cm⁻¹) to total Lewis acid sites (1221 and 1578 cm⁻¹). The results illustrate the amount of Lewis acid is 0.93, 0.69, 0.47, 0.31 and 0.28 mmol/g for CP120, CP140, CP160, CP180 and CP200, respectively, which exhibits a declining tendency from CP120 to CP200 with the increase in synthesized temperature. This can be ascribed to the hexagonal and monoclinic crystalline structure in CP120 and CP200, respectively. However, the amount of Brønsted acid for these catalysts do not exhibit obvious regularity, there is a

RSC Advances

decrease of Brønsted acid amount in CP140-CP180 catalysts (0.70-0.90 mmol/g). As we have known from XRD results, CP catalysts with different hydrothermal synthesis temperatures exhibit different crystallite types. CP140, CP160 and CP180 exhibit a mixture of two crystalline structures, which causes an unstable Brønsted acid site due to different surface properties. Moreover, IR spectra of CP120-CP140 and CP160-CP200 demonstrated different surface acid strength, which is in accordance with the result from NH₃-TPD (Fig. 4). **XPS measurement**

Published on 07 April 2016. Downloaded by Université Laval on 08/04/2016 08:10:16.

The CP catalysts were further analyzed by XPS to identify the surface nature and the results were shown in Fig. 6. The complex spectra of Ce3d were decomposed into eight components by Gaussian-Lorentz fitting procedure (Fig. 6). The sub-bands labeled v_1 and u_1 represented the $3d^{10}4f^{1}$ initial electronic state of Ce^{3+} , and the sub-bands labeled u_0 , u_2 , u_3 , v_0 , v_2 and v_3 represent the $3d^{10}4f^0$ state of Ce⁴⁺.^{39,40} The relative abundance of the Ce⁴⁺ (%) species of each sample was estimated by considering the deconvolution peak area of Ce3d binding energies. In Table 1, corresponding to the Ce⁴⁺ amount of these catalysts from CP120 to CP200 were 78%, 65%, 51%, 37% and 33%, respectively. As the synthesis temperature increased, the content of Ce⁴⁺ gradually reduced along from CP120 to CP200. As it has been reported Ce⁴⁺ provides Lewis acid site,³⁶ which means the decrease in the Ce⁴⁺ amount can lead to the decrease in the amount of Lewis acid site. Thus, CP120 shows the maximum Lewis acid amount that also certifies the DRIFT results. Fig. 7 gives a plot of Lewis acid amount (Table 1) versus the Ce⁴⁺ amount (Table 1) for the CP catalysts. It is interesting that a striking linearity is displayed between the Lewis acid amount and the Ce⁴⁺ amount of the CP catalysts (Fig. 7A). It was found that Lewis acid amounts decreased with the BET surface area (Table 1).

RSC Advances

Moreover, a near linearity relation was observed between Lewis acid amounts and BET surface area for CP catalysts (Fig. S1). Considering the effect of surface area, Lewis acid amounts on the basis of surface area were calculated for CP catalysts and shown in Table 1. Plot of surface Ce⁴⁺ amount versus Lewis acid amount on the basis of surface area (Table 1) for the CP catalysts were given (Fig. 7B). It was also found a linearity relation between surface Ce⁴⁺ amount and Lewis acid amount on the basis of surface area, which suggests that surface area plays a positive influence on the Lewis acid amount. Thus, the result proves that Lewis acid is related to the surface Ce⁴⁺ of the CP catalysts, and its amount is proportional to the content of surface Ce⁴⁺.

Catalytic performance

The catalytic performances of the CP catalysts were investigated for the dehydration of glucose to HMF displayed in Fig. 8. It was observed a lower than 1% conversion of glucose in this reaction without catalyst addition, which indicated a superior stability of glucose at this condition.⁴¹ From the Fig. 8, the conversion of glucose was 97%, 90%, 84%, 80% and 78% for CP120, CP140, CP160, CP180 and CP200, respectively, corresponding yields of HMF for these CP catalysts were 61%, 52%, 45%, 41% and 40%, respectively. It is easy to see that the yield of HMF and conversion of glucose decrease with the increase in synthesis temperature from CP120 to CP200. Among these CP catalysts, the CP120 catalyst has a preferable catalytic performance of conversion to glucose (97%) and yield to HMF (61%), which is better than most catalysts reported in literatures,^{12,20,23,42} such as SO_4^{2-}/ZrO_2 , SO_4^{2-}/ZrO_2 -Al₂O₃, niobia/carbon, aluminium doped MCM-41 silica and solid metal (IV) phosphate. Jiménez-López and co-workers reported the glucose conversion of 69% and HMF

RSC Advances

yield of 23 % were achieved at 175 °C over mesoporous tantalum oxide as catalyst.¹² Dibenedetto et al. used the same elements (Ce, P, O) to prepare different material of complex structures. These materials were used to catalyze fructose to HMF, the best yield to HMF (52%) was obtained, and the deactivation phenomenon was also observed.²⁷

As we have shown in Fig. 1, the structure of the CP catalysts changed from hexagonal (CP120) to monoclinic (CP200) with increase in synthesis temperature, along with the different catalytic performances. It indicates that the crystalline structure plays a noticeable influence on catalytic performance of the CP catalysts, which can be ascribed to the change of surface acidity with the modification of catalyst structure from hexagonal to monoclinic phase. Generally, the dehydration of glucose to HMF contains two stages: firstly, isomerization of glucose to fructose under Lewis acid sites, and then fructose dehydration to HMF over Brønsted acid.^{23,24} In order to study the stage, fructose dehydration to HMF was carried out over CP120 for 5, 10 and 15 min (Fig. S1). When the reaction time was 5 min, the conversion to fructose and selectivity to HMF could get about 93% and 49%, respectively. As the time increased to 10 min, the fructose almost converted completely, the conversion to fructose was 97%, corresponding 55% of selectivity to HMF. From the results, it can be found that the stage of fructose dehydration to HMF was very fast. In our previous report, it also confirmed that the dehydration of fructose to HMF was very fast over the carbon-based solid acid catalyst.⁴³ Moreover, compared it with glucose dehydration to HMF, the conversion to glucose and selectivity to HMF for the reaction time of 15 min under the same reaction conditions were only 66% and 40% (Fig. S2), respectively, which suggest that the reaction rate of glucose dehydration to HMF is slower than that of fructose dehydration to HMF. So, the

Published on 07 April 2016. Downloaded by Université Laval on 08/04/2016 08:10:16.

RSC Advances

View Article Online DOI: 10.1039/C6RA02602H

glucose isomerization to fructose is considered as the key rate determining step in the glucose dehydration to HMF. While, the isomerization of glucose to fructose is sensitive to Lewis acid in the initial stage of the glucose dehydration to HMF, so the modification of catalyst acidity will be very important for the reaction.

As it was mentioned, the structures of the CP catalysts changed from hexagonal (CP120) to monoclinic (CP200) phase, simultaneously, the crystal morphologies were converted from nanosphere (CP120) to nanorod (CP200) shape in accordance with the decrease of BET surface area. The CP catalysts exhibited specific surface acid sites of Lewis and Brønsted (Table 1). The Lewis acid of CP120 took up the highest content among all CP catalysts from Fig. 5 and Table 1, which showed somehow the best activity. From CP140 to CP200, Lewis acid amounts gradually reduced, they also displayed lower and lower activity for the dehydration of glucose with decrease in the amount of Lewis acid, even they had a large amount of Brønsted acid site. It is interesting that a striking linearity relation can be found between the conversion of glucose and the amount of Lewis acid for the CP catalysts (Fig. 9A). The relationship of selectivity to HMF versus the amount of Lewis acid also demonstrates the same situation as above described results (Fig. 9A). Considering the effect of surface area, plots of conversion to glucose and selectivity to 5-HMF versus Lewis acid amount on the basis of surface area (Table 1) for the CP catalysts were given, respectively (Fig. 9B). It was also found a very well linearity relation between conversion to glucose (selectivity to 5-HMF) and Lewis acid amount on the basis of surface area. These results can prove that the surface Lewis acid plays an important role in the dehydration of glucose to HMF.^{11,14} It also confirms that the isomerization of glucose to fructose is key stage in this

RSC Advances

reaction. In addition, Fig. 9B results also reveal positive influence of surface area on the catalytic activity of CP catalysts. Thus, the highest conversion (97%) and selectivity (63%) in CP120 was achieved, which should be accounted for the most amounts of Lewis acid sites and the highest surface area. But glucose cannot convert completely to HMF, which should be ascribed to the secondary processes of HMF rehydration process and condensation with sugars into humins.^{44,45}

More details of CP120 based on its excellent catalytic activity have been investigated in order to understand the effects of various experimental parameters to the reaction including reaction temperature, time, DMSO amount and ratio of glucose to catalyst.

Published on 07 April 2016. Downloaded by Université Laval on 08/04/2016 08:10:16.

Effect of temperature: Fig. 10 shows the effect of different reaction temperatures on catalytic activity. As illustrated in Fig. 10, a low HMF yield of 10% with the glucose conversion of 32% and HMF selectivity of 32% was obtained at reaction temperature of 130 °C. The conversion to glucose increased quickly from 32% to 95% with rising of reaction temperature from 130 °C to 150 °C. 97% conversion to glucose and 61% yield to HMF were obtained at 160 °C. It indicates that rising temperature is beneficial to glucose dehydration to HMF. However, when the temperature was increased further to 170 °C, the yield and selectivity of HMF gradually dropped to 60% accompanying slight increase in glucose conversion (near 100%), meanwhile the reaction solution gradually converted into a more dark color, which means formation of more humins⁴¹ that can cover on the active sites of catalyst surface. Furthermore, the selectivity of HMF showed similar trends as its yield, a better HMF selectivity of 63% was obtained at 160 °C. So 160 °C is much more proper than other temperature for this reaction.

RSC Advances

Effect of catalytic time: The impact of reaction time on activity has been explored as is shown in Fig. 11. The trend of activities has not shown a linearly increment by the extension of reaction time. When the reaction time was 15 min, the conversion (66%) was lower, that is maybe time is short and glucose cannot convert completely on the surface of catalyst. In the range of 30-60 min, conversion (95%-97%) and selectivity (57%-63%) displayed a moderate increase. When the reaction time increased to 90 and 120 min, tiny difference was obtained. Obviously to see the reduction of catalytic performance growth rate happens with the extension of reaction time. Apparently when the reaction time was longer than 60 min, it showed less effect on the property compared with that of shorter one (30-60 min). This can be attributed to the presence of products like humins which hinder the ongoing reaction process by covering the catalyst surface active site,⁴¹ meanwhile, the longer time reaction shows lower catalytic performance benefits. Consequently, 60 min is optimal time for this reaction.

Effect of the ratio of catalyst to glucose: The effect of the ratio of catalyst to glucose (g/g) on activity is shown in Fig. 12. The amount of CP120 was 50 mg and dosage of glucose was increased from 50 mg to 250 mg to change the ratio of catalyst to glucose from 1:1 to 1:5. It is notable to see that the conversion was almost unchanged with the increase in the amount of glucose, however, HMF selectivity showed obviously a different tendency. When the ratio of catalyst to glucose decreased from 1:1 to 1:4, HMF selectivity gradually increased from 41% to 62%, however, when the ratio was 1:5, the selectivity of HMF appeared to decrease rapidly to 43%, which in turn also made HMF yield down to 41%. When the amount of catalyst is too much, it will make an interaction between glucose and new generated HMF on catalyst surface, which leads to lower HMF selectivity due to formation of the formic, levulinic acids

RSC Advances

and humins.⁴¹ But the less amount of catalyst cannot completely catalyze the reaction. From the above result, the conclusion can be made like that optimum ratio of catalyst to glucose in this reaction is 1:4.

Effect of DMSO amount: It was reported that DMSO had an effective influence on improvement of HMF yield by their extractability to suppress undesired by-product and sequentially increase the selectivity of 5-HMF.⁴⁶⁻⁴⁹ Here, the effect of DMSO amount was also investigated in this reaction as the results shown in Fig. 13. From the results, it is easy to see that 5 ml solvent showed a negative effect toward glucose conversion which displayed a minimum HMF yield (40%). When increasing the solvent amount to 10 ml, a obvious increment of HMF yield (from 40% to 61%) was observed, however, further increasing the amount of solvent did not improve reaction activity even cost the loss of HMF selectivity from 62% to 46%, product yield decreased from 61% to 41%, all these results indicate that much more solvent amount (the optimum is 10 ml as shown above) will reduce the contact with the substrate and decrease the reactant concentration and in turn decreased the reaction activity. Therefore, 10 ml DMSO has been taken for dehydration of glucose to HMF in this study.

Published on 07 April 2016. Downloaded by Université Laval on 08/04/2016 08:10:16.

As the results are presented in Fig. 10, 11, 12 and 13, which suggest that CP120 catalyst shows an excellent catalytic performance for glucose dehydration to 5-hydroxymethylfurfural in the condition of 50 mg catalyst, 200 mg glucose, 160 °C, 60 min and 10 ml DMSO as solvent.

Reusability: The stability of the CP120 catalyst was also tested based on its excellent catalytic activity for glucose dehydration to 5-HMF. After the reaction was completed and

RSC Advances

filtered, used CP120 was washed with methanol and DMSO, and then dried at 100 °C for 12 h, labeled as CP120-used-1 and CP120-used-2 for first and second reused cycle, respectively. The reusability test results are showed in Fig. 14. It can be seen that the yield of fresh CP120 was about 54% and the glucose conversion was 95%. After first and second cycle, the activity reduced obviously. The yield of HMF decreased from 54% to 33%, indicating that the catalyst partially deactivated during the recycling process. In this reusability reaction, the activity of CP120-used-1 declined much more than that of CP120-used-2. After first reused cycle, CP120-used-1 demonstrated 14% lower yield of HMF than the fresh CP120. The glucose conversion decreased from 85% to 75% was founded in the second used cycle, in which the selectivity of HMF only showed a tiny decrease from 47% to 45%, which indicated that the deactivation was not obvious after the first used cycle. XRD pattern of CP120-used-1 (Fig. S3) showed 2θ sites of the diffraction peaks were not obvious alteration and only displayed a decrease in crystalline compared with CP120, indicating the hexagonal structure of CP120-used-1 was still maintained. Moreover, a reaction solution was obtained by hot filtration, and glucose was added into the above solution to assess if any leaching of active catalytic species into the solution. The result indicates that there is no activity in this reaction solution at the same conditions. So the active catalytic species are not leach into the reaction solution. In addition, it was noticed that the used CP-120 color changed into dark due to formation of by-product humans that can cover up of surface acid site leading to catalyst deactivation according to literatures.^{41,44,45}

Conclusions

A series of CePO₄ catalysts with hexagonal and/or monoclinic CePO₄ crystal types have

RSC Advances

been successfully synthesized by hydrothermal method. The increase in hydrothermal temperature exchange catalyst crystal phase gradually from hexagonal to monoclinic, which lead to change of BET surface area and acidity. Catalytic performance combined with characterization results suggest that surface acid strength and the distribution of different acid site type influence the catalyst activity significantly. The amount of Lewis acid based on either catalyst mass or surface area increases with the content of surface Ce⁴⁺ among these CP catalysts, which shows a striking linearity between them. A very well linearity is also displayed between Lewis acid amount based on either catalyst mass or surface area and conversion of glucose and selectivity of HMF. Therefore, we put forward to Lewis acid plays a key role in dehydration of glucose to HMF, which is derived from the surface Ce^{4+} of the CP catalysts. The best catalytic performance is obtained over CP120 nanoparticles with 30-60 nm in the dehydration of glucose to HMF, which exhibits a HMF yield of 61% at the glucose conversion of 97% using 10 ml DMSO as solvent, 50 mg catalyst and 200 mg glucose at 160 °C for 60 min. It is attributed to the most amount of Lewis acid and the highest BET surface area among these CP catalysts.

Acknowledgements

Published on 07 April 2016. Downloaded by Université Laval on 08/04/2016 08:10:16.

This work was supported by Natural Sciences Fund of Heilongjiang Province (B2015009), Postdoctoral Science-research Developmental Foundation of Heilongjiang Province of China (LBH-Q12022), Program for Innovative Research Team in University (IRT-1237), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (2013-1792) and Ministry of Human Resources and Social Security (2013-277), Innovative Research Project of Key Laboratory of Functional Inorganic Material Chemistry,

Ministry of Education.

References

- 1. B. Saha and M. M. Abu-Omar, Green Chem., 2014, 16, 24-38.
- 2. S. P. Teong, G. Yi and Y. Zhang, Green Chem., 2014, 16, 2015-2026.
- 3. E. R. Sacia, M. Balakrishnan and A. T. Bell, J. Catal., 2014, 313, 70-79.
- L. Hu, G. Zhao, W. Hao, X. Tang, Y. Sun, L. Lin and S. Liu, *RSC Adv.*, 2012, 2, 11184-11206
- 5. T. Wang, M. W. Nolte and B. H. Shanks, Green Chem., 2014, 16, 548-572.
- 6. W. Deng, Q. Zhang and Y. Wang, Sci. China Chem., 2014, 58, 29-46.
- 7. H. Cai, C. Li, A. Wang, G. Xu and T. Zhang, Appl. Catal. B, 2012, 123-124, 333-338.
- 8. X. Tong, Y. Ma and Y. Li, Appl. Catal. A, 2010, 385, 1-13.
- 9. M. J. Climent, A. Corma and S. Iborra, Green Chem., 2011, 13, 520.
- J. Zhou, Z. Xia, T. Huang, P. Yan, W. Xu, Z. Xu, J. Wang and Z. C. Zhang, *Green Chem.*, 2015, 17, 4206-4216.
- A. Osatiashtiani, A. F. Lee, D. R. Brown, J. A. Melero, G. Morales and K. Wilson, *Catal. Sci. Technol.*, 2014, 4, 333-342.
- I. Jiménez-Morales, M. Moreno-Recio, J. Santamaría-González, P. Maireles-Torres and A. Jiménez-López, *Appl.Catal. B*, 2014, **154-155**, 190-196.
- 13. X. Qi, M. Watanabe, T. M. Aida and R. L. S. Jr, Catal. Commun., 2009, 10, 1771-1775.
- 14. M. Zhang, K. Su, H. Song, Z. Li and B. Cheng, Catal. Commun., 2015, 69, 76-80.
- V. V. Ordomsky, J. v. d. Schaaf, J. C. Schouten and T. A. Nijhuis, *J. Catal.*, 2012, 287, 68-75.

- 16. M. Dashtban, A. Gilbert and P. Fatehi, RSC Adv., 2014, 4, 2037-2050.
- 17. Y. Yang, C. Hu and M. M. Abu-Omar, J. Mol. Catal. A, 2013, 376, 98-102.
- 18. Z. Zhang and Z. K. Zhao, Bioresour Technol., 2011, 102, 3970-3972.
- 19. H. Jadhav, E. Taarning, C. M. Pedersen and M. Bols, *Tetrahedron Lett.*, 2012, 53, 983-985.
- R. Weingarten, Y. T. Kim, G. A. Tompsett, A. Fernández, K. S. Han, E. W. Hagaman,
 W. C. C. Jr, J. A. Dumesic and G. W. Huber, *J. Catal.*, 2013, **304**, 123-134.
- 21. M. I. Alam, S. De, B. Singh, B. Saha and M. M. Abu-Omar, *Appl.Catal. A*, 2014, **486**, 42-48.
- 22. R. Gounder and M. E. Davis, J. Catal., 2013, 308, 176-188.

- 23. H. Yan, Y. Yang, D. Tong, X. Xiang and C. Hu, Catal. Commun., 2009, 10, 1558-1563.
- T. D. Swift, H. Nguyen, Z. Erdman, J. S. Kruger, V. Nikolakis and D. G. Vlachos, J. Catal., 2016, 333, 149-161.
- 25. S. Xu, X. Yan, Q. Bu and H. Xia, RSC Adv., 2016, 6, 8048-8052
- 26. L. Yang, X. Yan, S. Xu, H. Chen, H. Xia and S. Zuo, RSC Adv., 2015, 5, 19900-19906
- A. Dibenedetto, M. Aresta, C. Pastore, L. di Bitonto, A. Angelini and E. Quaranta, RSC Adv., 2015, 5, 26941-26948.
- 28. A. Sinhamahapatra, N. Sutradhar, B. Roy, A. Tarafdar, H. C. Bajaj and A. B. Panda, *Appl. Catal. A*, 2010, **385**, 22-30.
- 29. J. Bao, R. Yu, J. Zhang, X. Yang, D. Wang, J. Deng, J. Chen and X. Xing, CrystEngComm., 2009, 11, 1630-1634.
- 30. K. Rajesh, P. Mukundan, P. K. Pillai, V. R. Nair and K. G. K. Warrier, Chem. Mater.,

2004, 16, 2700-2705.

- 31. R. Amrousse, A. Tsutsumi, A. Bachar and D. Lahcene, *Appl. Catal. A*, 2013, **450**, 253-260.
- 32. L. Ho, H. Nishiguchi, K. Nagaoka and Y. Takita, Mater. Chem. Phys., 2006, 97, 494-500.
- 33. M. Choi, R. Srivastava and R. Ryoo, Chem. Commun., 2006, 42, 4380-4382.
- 34. M. A. Larrubia, G. Ramis and G. Busca, Appl. Catal. B, 2000, 27, L145-L151.
- 35. A. Trovarelli, Catal. Rev., 2006, 38, 439-520.
- 36. L. Chen, J. Li and A. M. Ge, Environ. Sci. Technol., 2010, 44, 9590-9596.
- Z. Wu, B. Jiang, Y. Liu, H. Wang and A. R. Jin, *Environ. Sci. Technol.*, 2007, 41, 5812-5817.
- 38. W. S. Kijlstra, D. S. Brands, E. K. Poels and A. Bliek, J. Catal., 1997, 171, 208-218.
- 39. M. Piumetti, S. Bensaid, N. Russo and D. Fino, Appl. Catal. B, 2015, 165, 742-751.
- 40. P. Maitarad, J. Han, D. Zhang, L. Shi, S. Namuangruk and T. Rungrotmongkol, *J. Phys. Chem. C*, 2014, **118**, 9612-9620.
- V. V. Ordomsky, V. L. Sushkevich, J. C. Schouten, J. van der Schaaf and T. A. Nijhuis, J. Catal., 2013, 300, 37-46.
- 42. H. Xiong, T. Wang, B. H. Shanks and A. K. Datye, Catal. Lett., 2013, 143, 509-516.
- 43. C. Wang, F. Yuan, L. Liu, X. Niu and Y. Zhu, ChemPlusChem., 2015, 80, 1657-1665
- 44. V. V. Ordomsky, J. van der Schaaf, J. C. Schouten and T. A. Nijhuis, *ChemSusChem.*, 2012, **5**, 1812-1819.
- 45. B. F. M.Kuster, Carbohyd. Res., 1977, 54, 177-183.
- 46. Y. Wang, Z. Gu, W. Liu, Y. Yao, H. Wang, X. Xia and W. Li, RSC Adv., 2015, 5,

60736-60744

- 47. C. B. Rasrendra, J. N. M. Soetedjo, I. G. B. N. Makertihartha, S. Adisasmito and H. J. Heeres, *Top. Catal.*, 2012, **55**, 543-549.
- 48. R. M. Musau and R. M. Munavu, Biomass, 1987, 13, 67.
- 49. Y. Yang, W. Liu, N. Wang, H. Wang, Z. Song and W. Li, RSC Adv., 2015, 5, 27805-27813

Catalyst	SA(m ² /g)	PV(cm ³ /g)	Total Acidity	otal Acidity NH_3 adsorption (mmol/g) ^b		Lewis acid	$Ce^{4+}/(Ce^{3+}+Ce^{4+})^{d}$
			(mmol/g) ^a	Brønsted (B)	Lewis (L)	$(\mu mol/m^2)^{c}$	(%)
CP120	108	0.39	1.67	0.74	0.93	8.6	78
CP140	88	0.39	1.39	0.70	0.69	7.8	65
CP160	82	0.36	1.29	0.82	0.47	5.7	51
CP180	65	0.30	1.21	0.90	0.31	4.8	37
CP200	54	0.26	0.79	0.51	0.28	5.2	33

Table 1 physicochemical properties of the CP catalysts

a. Calculated from the NH₃-TPD

b. Calculated from the NH₃-TPD and DRIFT based on catalyst mass

c. Lewis acid amount based on special surface area

d. Calculated from the XPS



Scheme 1 reaction pathway for glucose to HMF

Figures Captions

Fig. 1 XRD patterns of the CP catalysts (A: CP120, B: CP140, C: CP160, D: CP180, E: CP200)

CP140, C: CP160, D: CP180, E: CP200)

Fig. 3 SEM images of A: CP120, B: CP160, C: CP200

Fig. 5 DRIFT spectra of the CP catalysts (A: CP120, B: CP140, C: CP160, D: CP180, E: CP200)

Fig. 6 XPS of the CP catalysts (A: CP120, B: CP140, C: CP160, D: CP180, E: CP200)

Fig. 7 plots of A: Lewis acid amount based on catalyst mass (mmol/g) and B: Lewis acid amount based on surface area (μ mol/m²) versus Ce⁴⁺ amount for the CP catalysts

Fig. 8 activity of the dehydration of glucose over the CP catalysts (HMF yield, glucose conversion, HMF selectivity; Reaction conditions: Glucose: 200 mg, catalyst: 50 mg, solvent: 10 ml DMSO, temperature: 160 °C)

Fig. 9 plots of conversion to glucose and selectivity to 5-HMF versus A: Lewis acid amount based on catalyst mass (mmol/g) and B: Lewis acid amount base on surface area (μ mol/m²) for the CP catalysts

Fig. 10 effect of temperature on the dehydration of glucose over CP120 (HMF yield, glucose conversion, HMF selectivity; Reaction conditions: Glucose: 200 mg, catalyst: 50 mg, solvent: 10 ml DMSO, time: 30 min)

Fig. 11 effect of reaction time on the dehydration of glucose over CP120 (HMF yield, glucose conversion, HMF selectivity; Reaction conditions: Glucose: 200 mg, catalyst: 50 mg, solvent: 10 ml DMSO, temperature: 160 °C)

Fig. 12 effect of the ratio of catalyst to glucose (g/g) on the dehydration of glucose over CP120 (HMF yield, glucose conversion, HMF selectivity; Reaction conditions: Glucose: 200 mg, solvent: 10 ml DMSO, temperature: 160 °C)

Fig. 13 effect of the solvent amount on the dehydration of glucose over CP120 (HMF yield, glucose conversion, HMF selectivity; Reaction conditions: Glucose: 200 mg, catalyst: 50 mg, DMSO, temperature: 160 °C)

Fig. 14 reusability on the dehydration of glucose over CP120 (HMF yield, glucose conversion, HMF selectivity; Reaction conditions: Glucose: 200 mg, catalyst: 50 mg, solvent: 10 ml DMSO, time: 30 min temperature: 160 °C)



Fig. 1 XRD patterns of the CP catalysts (A: CP120, B: CP140, C: CP160, D: CP180, E: CP200)



Fig. 2 N₂ adsorption-desorption isothermals (a) and pore distribution (b) of the CP catalysts (A: CP120, B: CP140, C: CP160, D: CP180, E: CP200)



Fig. 3 SEM images of A: CP120, B: CP160, C: CP200



Fig. 4 NH₃-TPD profiles of the CP catalysts (A: CP120, B: CP140, C: CP160, D: CP180, E: CP200)



Fig. 5 DRIFT spectra of the CP catalysts (A: CP120, B: CP140, C: CP160, D: CP180, E: CP200)



Fig. 6 XPS of the CP catalysts (A: CP120, B: CP140, C: CP160, D: CP180, E: CP200)



Fig. 7 plots of A: Lewis acid amount based on catalyst mass (mmol/g) and B: Lewis acid amount based on surface area (μ mol/m²) versus Ce⁴⁺ amount for the CP catalysts



DMSO, temperature: 160 °C)



Fig. 9 plots of conversion to glucose and selectivity to 5-HMF versus A: Lewis acid amount based on catalyst mass (mmol/g) and B: Lewis acid amount base on surface area (μ mol/m²) for the CP catalysts



Fig. 10 effect of temperature on the dehydration of glucose over CP120 (HMF yield, glucose conversion, HMF selectivity; Reaction conditions: Glucose: 200 mg, catalyst: 50 mg, solvent: 10 ml DMSO, time: 30 min)



Fig. 11 effect of reaction time on the dehydration of glucose over CP120 (HMF yield, glucose conversion, HMF selectivity; Reaction conditions: Glucose: 200 mg, catalyst: 50 mg, solvent: 10 ml DMSO, temperature: 160 °C)



Fig. 12 effect of the ratio of catalyst to glucose (g/g) on the dehydration of glucose over CP120 (HMF yield, glucose conversion, HMF selectivity; Reaction conditions: Glucose: 200 mg, solvent: 10 ml DMSO, temperature: 160 °C)



Fig. 13 effect of the solvent amount on the dehydration of glucose over CP120 (HMF yield, glucose conversion, HMF selectivity; Reaction conditions: Glucose: 200 mg, catalyst: 50 mg, DMSO, temperature: 160 °C)



Fig. 14 reusability on the dehydration of glucose over CP120 (HMF yield, glucose conversion, HMF selectivity; Reaction conditions: Glucose: 200 mg, catalyst: 50 mg, solvent: 10 ml DMSO, time: 30 min temperature: 160 °C)

39

Published on 07 April 2016. Downloaded by Université Laval on 08/04/2016 08:10:16.

Graphical Abstract

Effect of Cerous Phosphates with Different Crystal Structures on Their Acidity and Catalytic Activity for Dehydration of Glucose into 5-(hydroxymethyl)furfural

Lina Wang, Fulong Yuan, Xiaoyu Niu, Chuanhong Kang, Pengying Li, Zhibin Li*, Yujun Zhu*

Cerous phosphates catalysts with different crystal structures show different catalytic performance for the dehydration of glucose into 5-hydroxymethylfulural due to their surface Ce⁴⁺ amount and acidity.

