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View Article Online
DOI: 10.1039/C5RA11411J

Journal Name

ARTICLE

# Catalytic dehydration of D-xylose to furfural over a tantalum-based catalyst in batch and continuous process†

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Furfural is a biomass-based bulk chemical and its derivatives have potential applications as renewable fuels and chemicals. A water-tolerant and stable solid acid catalyst modified hydrated tantalum oxide (TA-p) was developed for catalytic conversion of D-xylose to furfural in water-organic solvent biphasic system. This process was performed both in a batch reactor and a continuous fixed-bed reactor. In the batch process, D-xylose conversion and furfural yield were significantly affected by the organic solvent, reaction temperature and reaction time. 1-Butanol, which could be obtained through the fermentation of biomass-based carbohydrates, was selected as organic phase and the highest furfural yield of 59% was achieved with D-xylose conversion of 96% at 180 °C in the continuous process. Moreover, the long-time stability test for 80 h under the optimal conditions showed the excellent stability of TA-p catalyst.

## 1.Introduction

Biomass resource is the only renewable resource which can be converted into liquid transportation fuels and chemicals.[1] Carbohydrates accounted for a large proportion in the biomass resources and the efficient conversion of carbohydrates (especially $C_5$, $C_6$ sugars) to fuels and chemicals is a promising way to solve the crisis of fossil resources and environmental problems.[2] Pentose, mainly D-xylose, was obtained by the hydrolysis of hemicellulose in the biomass. Furfural, produced from pentose, is a biomass-based bulk chemical.[3] The derivatives converted from furfural have potential applications as fuels, polymers, pharmaceutical intermediates and pesticides.[4] More importantly, furfural could be hydrogenated to a range of potential fuel alternatives such as methyltetrahydrofuran.[5] Therefore, the efficient conversion of pentose into furfural is a key process in the biomass conversion.[6]

Conventional catalysts for the conversion of D-xylose to furfural were inorganic acids, such as sulfuric acid and hydrochloric acid.[7] However, these inorganic acids caused a series of problems which included serious corrosion, toxicity, environmental pollution, difficulties in product separation and side reactions, leading to lower yield of furfural. In order to minimize the loss of furfural through secondary reactions and simultaneously removing of furfural from the reacting medium in which superheated steam was used as the stripping agent.[4a] Alternatively the catalysts were replaced by acetic acid superphosphate, methanesulfonic acid or sulfate salts.[4b, 4c, 8] However, its usual yield is still around 50%. These conditions showed several drawbacks: high vapor product dilution leading to expensive purification stages, safety issues and environmental problems due to toxic waste effluents. Then ionic liquids as novel and green solvents were applied to the dehydration of monosaccharide to furfural.[9] However, due to potential drawback of the cost, the process using ionic liquids was probably not suitable for economically scalable production of furfural. For these reasons, the improvement of appropriate chemical technology remains great interest for the growth of furan-based industry.

At present, the development of stable, efficient and non-toxic solid acid catalysts used in the furfural production to replace the traditional inorganic acid catalysts is a research issue.[10] Recently, some solid acid catalysts, e.g. Sn-Beta,[11] H-Beta,[12] Sn-MMT,[13] $SO_4^{2-}/SnO_2$,[14] $SO_4^{2-}/TiO_2$-$ZrO_2$/La,[15] P-C-$SO_3H$,[16] ion exchange resin like Amberlyst and Nafion,[17] supported- phosphotungstate,[18] zeolites,[19] modified SBA-15,[20] $TiO_2$/RGO and $TiO_2$/CB,[21] niobia catalysts,[22] $Cr_2O_3$-HT,[23] $WO_3/SiO_2$,[24] $SiO_2$-PSSA,[25] TMG·$HSO_4$[26] were used for the dehydration of D-xylose to furfural.

In order to avoid the undesired side reaction generating humins and improve the selectivity of product, the solvent system of the process was developed from the traditional single-phase system [27] to biphasic system containing water and organic solvent. Accordingly, the separation process of the product had also been simplified when the water-immiscible organic solvent biphasic system was used. The reported organic solvents in biphasic system included methyl isobutyl ketone (MIBK),[28] toluene,[29] 2-methyltetrahydrofuran (2-MTHF)[30], dimethylsulfoxide (DMSO)[31] and 1-butanol[19b]. In particular, the alcohols prepared by the fermentation of biomass-based carbohydrates were considered to be the potential solvents in

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† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x.

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DOI: 10.1039/C5RA11411J

future.[32] In this respect, it will be of significance to develop water-tolerant and stable heterogeneous catalysts used in this process. To this end, niobium oxide and tantalum compounds, which have acidic properties and are insoluble in water, exhibit high activity in the dehydration of saccharides to 5-hydroxymethylfurfural.[33] Additionally, the conversion of D-xylose to furfural catalysed by solid acid catalysts in biphasic system was mainly performed in batch process, whereas the in-depth study of continuous process was rarely involved. However, continuous process has the advantage of lower cost in the procedures of operation and separation and more suitable for large-scale production. Thus, the development of continuous process is of great significance.

In this work, modified hydrated tantalum oxide (TA-p) was investigated as a water-tolerant solid acid catalyst for the production of furfural from D-xylose by using a biphasic system containing water and 1-butanol. This process was performed both in a batch reactor and a continuous fixed-bed reactor. The catalyst exhibited high activity and excellent stability in continuous flow fixed-bed reactor. The effects of different parameters on the catalytic performance in the batch and continuous process were evaluated. The time-on-stream experiment for 80 h was performed to show the stability of the catalyst.

## 2. Experimental

### 2.1. Preparation of catalyst

The reagents used in preparation of catalyst and reactions were commercially available and analytically pure (AR). D-xylose was purchased from Aladdin-Reagent Inc. (China) and furfural was purchased from Sinopharm Chemical Reagent Co., Ltd (China). Modified hydrated tantalum oxide (TA-p) was prepared according to the literature[33a], and the details were as follows:

100 g of commercially available hydroxide tantalum ($Ta_2O_5·nH_2O$, TA, HKXC, China) was added to 1.5 L 10% phosphoric acid solution (v/v, 100 mL of concentrated phosphoric acid in 1.4 L of water) and stirred at room temperature for 52 h. Then the mixture was aged for 12 h at ambient condition. After aging, the precipitate was washed 5 times with deionized water to remove the acid until the pH was neutral and dried at 65 ºC overnight, followed by drying at 110 ºC in vacuum for 2 h. The catalyst was calcined in air at 300 ºC for 3 h with a heating rate of 2 ºC /min. 75 g of white powder was obtained.

### 2.2. Characterization of catalyst

The surface areas were determined at Tristar II 3020 (Micromeritics Instrument Corporation) by Brunauer-Emmett-Teller (BET) isotherms of $N_2$ adsorption at -196 ºC. $NH_3$-Temperature Programmed Desorption ($NH_3$-TPD) studies were carried out in a quartz tube reactor with a thermal conductivity detector (TCD). 100 mg of catalyst was loaded in a quartz tube and ammonia was adsorbed onto the catalyst for 2 h at 100 ºC. Subsequently, the sample was heated at a rate of 10 ºC /min to 700 ºC and a helium flow rate of 30 mL/min. Thermal analysis (TG-DSC, Thermo gravimetric-Differential Scanning Calorimeter) of TA-p was conducted with a Q5000IR Thermo Gravimetric Analyzer (TA Instrument) in $N_2$ (50 mL/min) from room temperature to 800 ºC at a heating rate of 10 ºC /min. Fourier transform infrared spectroscopy (FTIR) spectra of TA and TA-p were recorded on a Fourier transform instrument Nicolet 8700 (Thermo Scientific), using pressed disks of KBr. The powder X-ray diffraction (XRD) pattern of the TA-p was collected with an X'pert (PANalytical) diffractometer at 40 kV and 40 mA, using Ni-filtered Cu-Kα radiation. 2θ was in a range of 10 ° ~ 70 °.

### 2.3. The conversion process of D-xylose to furfural

A typical batch procedure was performed as follows: 0.4 g of D-xylose, 400 mg of TA-p catalyst, 4 mL of water and 6 mL of organic solvent were added into 25 mL autoclave at ambient condition. The reactor was sealed and heated to 160 ºC for 3 h. After reaction, the mixture was cooled to room temperature. The sample was diluted and filtered by a hydrophilic microporous membrane (22 μm). The filtrate was analysed by high performance liquid chromatography (HPLC) and D-xylose conversion and furfural yield were calculated.

Continuous process of converting D-xylose to furfural was performed in a fixed-bed reactor, using a biphasic system in which the aqueous phase was 100 g/L aqueous solution of D-xylose and the organic phase was 1-butanol. The fixed-bed reactor was equipped with a zirconium reaction tube with an inner diameter of 8 mm, in which the catalyst granules (20-40 mesh) were loaded to the volume of 3 mL. The fixed-bed reactor was mounted inside a heating furnace and heated to 180 ºC. The system pressure was controlled by the back pressure valve (Swagelok, USA). The reaction temperature was detected by the K-type thermocouples and controlled by AI-518P temperature controllers (YuDian Tech Co. Ltd. China). Before feeding the reagents, the system was filled with nitrogen to a pressure of 2.0 MPa. The aqueous solution of D-xylose and the organic phase of 1-butanol were constituted into the dynamic mixer at a certain flow rate by two SSI pumps (USA). The mixtures flowed through the catalyst bed which was heated to 180 ºC. The effluent was cooled and collected in a gas-liquid separator. The liquid products were sampled then the aqueous phase and 1-butanol phase were separated. The sample was diluted and filtered by a hydrophilic microporous membrane (22 μm). The concentrations of furfural and D-xylose in the organic and aqueous phases were determined by HPLC.

Liquid hourly space velocity (LHSV) = (the volume of 10 wt% aqueous solution of D-xylose pumped into the fixed bed per hour + the volume of 1-butanol pumped into the fixed bed per hour) / the volume of the catalyst loaded in the reactor.

### 2.4. Analysis method

The concentration of furfural was determined by HPLC using external standard method. HPLC was performed with a Hitachi L-2000 HPLC system equipped with two L-2130 pumps and an L-2455 photodiode array detector. Furfural was analyzed by reversed-phase chromatography on an Alltech $C_{18}$ packed column (250×4.6 mm, Alltech) at a column temperature of 30 ºC. The flow of mobile phase was methanol and water (methanol/water = 20:80) at a flow rate of 1.0 mL/min. The detection wavelength of furfural was 2[illegible]7 nm. The concentration of D-xylose was determined by HPLC using external standard method. HPLC was performed with a Hitachi L-

2000 HPLC system equipped with two L-2130 pumps and an Alltech evaporative light scattering detector (ELSD). D-xylose was analyzed by Necelai Cosmail Sugar-D column (250×4.6 mm, Necelai) at a column temperature of 30 °C. The flow of mobile phase was acetonitrile and water (acetonitrile/water = 75:25) at a flow rate of 1.0 mL/min. D-xylose conversion was calculated from the aqueous phase concentration in the product determined by the HPLC and the aqueous phase volume after reaction, and furfural yield was calculated from the aqueous and organic phase concentration in the product determined by the HPLC and their corresponding volumes since the volumes changed after reaction.

The conversion of D-xylose, the selectivity and yield of furfural were defined as follows:

Conversion = (moles of reacted D-xylose) / (moles of initial D-xylose) ×100%
Yield =(moles of produced furfural) / (moles of initial D-xylose) ×100%
Selectivity =(moles of produced furfural) / (moles of reacted D-xylose) ×100%

## 3. Results and discussion

### 3.1. Characterization of the catalyst TA-p

The acidities of the catalysts were measured by $NH_3$-TPD experiments and BET surface areas were determined by $N_2$ isothermal (-196 °C) adsorption (Table 1).

Table 1. The effect of calcination temperature on the acid density and catalytic activity of TA-p.[a]

| Entry | Catalyst | BET $/m^2\cdot g^{-1}$ | Acid density/ $mmol\cdot g^{-1}$ | Conversion of D-xylose (%) | Yield of furfural (%) |
|---|---|---|---|---|---|
| 1 | TA | 40.5 | 0.8 | 78.2 | 32.5 |
| 2 | TA-p-300 | 139.6 | 1.6 | 89.8 | 48.3 |
| 3 | TA-p-500 | 90.3 | 1.0 | 58.2 | 28.6 |
| 4 | TA-p-700 | 36.7 | 0.4 | 35.7 | 17.1 |
| 5 | TA-p-900 | 12.1 | 0.1 | 22.5 | 8.9 |

[a] Conditions: TA: hydroxide tantalum, TA-p-300 correspond to TA reacted with 1 mol/L phosphoric acid and calcined at 300 °C. Acid density was measured by $NH_3$-TPD. Conversion of D-xylose and yield of furfural were calculated by HPLC. Reaction condition: 0.4 g of D-xylose, 400 mg of catalyst, 4 mL of water and 6 mL of 1-butanol, 160 °C, 3 h.

Although hydroxide tantalum ($Ta_2O_5\cdot nH_2O$, TA, hydrated tantalum oxide) exhibited acid properties and had catalytic activity in the conversion of D-xylose into furfural (Table1, Entry 1), TA-p-300 (TA reacted with 1 mol/L phosphoric acid and calcined at 300 °C) displayed stronger acidity and higher catalytic activity (Table1, Entry 2). The calcination temperature had an obvious effect on the acid density and catalytic activity of TA-p (Table 1, Entry 2-5). Compared to the TA-p-500 and TA, the former has more acidity and surface area than that of TA. But the TA-p-500 is less activity than TA. This may be due to the formation of pyrophosphates which reduced the activity of catalyst.[34] Higher calcination temperature decreased BET surface area and acid density of TA-p, leading to a lower catalytic activity in reaction. A possible explanation was that the crystallite size of TA-p became larger qualitatively with the increase of the calcination temperature, resulting in a decrease of BET surface area and acid density. This explanation was consisted with the XRD patterns of the catalyst TA-p at different calcination temperature (Supplemental Fig. S1). When the calcination temperature was below 700 °C, TA-p was mainly in the amorphous form and had strong acidity and high catalytic activity. Correspondingly, powder XRD patterns of TA-p calcined at 900 °C exhibited intense diffraction peaks in the 2θ range of 10°~70°. Summarizing the results from above different characterization techniques, TA-p calcined at 300 °C was chose as a suitable catalyst for further characterizations and the conversion of D-xylose.

TG-DSC curves were measured from room temperature to 800 °C (Supplemental Fig. S2). No obvious decomposition of the catalyst indicated a good thermal stability. Also, compared to TA, the stretching vibration peak of $PO_4^{3-}$ at the wavenumber of 904 $cm^{-1}$ in the FTIR spectra of TA-p indicated the presence of $PO_4^{3-}$ (Supplemental Fig. S3).[35] The IR peaks at 3416.3 $cm^{-1}$、3173.8 $cm^{-1}$ 、1624.7 $cm^{-1}$、1403.2 $cm^{-1}$ and 614.2 $cm^{-1}$ are belong to tantalic acid.[36] Bands at 1624.7 $cm^{-1}$ and 3416.3 $cm^{-1}$ are attributed to the stretching of OH groups in water. The peak intensity of the phosphate modified catalyst at 1624.7 $cm^{-1}$ was decreased indicated the decrease of the catalyst surface hydroxyl groups. This can also be corroborated in the TG-DSC (Fig. S2) that the catalyst has a partial loss in the rise from room temperature to 300 °C.[37] The characteristic peak at 936.6 $cm^{-1}$ in the modified catalyst, which is not present in the tantalum acid, may be the formation of the Ta-O-P structure.[38] The peaks at 614.2 $cm^{-1}$, 757.1 $cm^{-1}$ and 830.6 $cm^{-1}$ are attribute to Ta-O or Ta-O-Ta.[39] The broad and intense band centred at 1057.4 $cm^{-1}$ may contain both the stretching of phosphate groups and the stretching vibrations of Ta=O groups.[39a]

### 3.2. Batch process of D-xylose conversion to furfural

The batch process was performed in the water–organic solvent biphasic system. Initially, the blank experiments without catalyst were performed in six different organic solvents: 1-butanol(1-BA)，2-butanol (2-BA), methyl isobutyl ketone (MIBK), iso-amyl alcohol (i-AA), methyl tert-butyl ether (MTBE) and methyl isobutyl carbinol (MIBC). Aqueous solution of D-xylose and the organic solvent (water: the organic solvent = 1:1.5 v/v) were stirred at 160 °C for 3 h. The results of the blank experiments showed that furfural yield did not exceed 5% in six different organic solvents in the absence of the catalyst TA-p (Supplemental Fig. S4). The selectivity to furfural was also poor (9 ~ 20%) with low conversion of D-xylose (19 ~ 30%).

After the blank experiments, the effects of the reaction temperature and organic solvents on conversion of D-xylose and yield of furfural were studied in the presence of TA-p. The process was performed in six different organic solvents at 140 °C, 160 °C and 180 °C, respectively (Fig. 1 A, B and C). The results showed that

TA-p had a remarkable catalytic effect on the dehydration of D-xylose. Obviously, the conversion of D-xylose significantly increased as the temperature rose from 140 ºC to 180 ºC, and D-xylose was converted almost completely at 180 ºC in all the six organic solvents. The yields of furfural increased initially (from 140 ºC to 160 ºC) and then decreased (from 160 ºC to 180 ºC) in 1-butanol, i-AA, MTBE, and especially in MIBC, and thus the highest yield of furfural was achieved at 160 ºC. Moreover, increasing reaction temperature led to the increase of furfural yield in 2-BA and MIBK from 140 ºC to 180 ºC. But the yield of furfural wasn’t increased obviously from 160 ºC to 180 ºC. This may be due to the increased formation of humins along with the increased temperature. We found that different solvent systems have different trends in the selectivity of furfural with the increased temperature. For alcohol solvent, the conversion of xylose increased whereas furfural yield slightly decreased from 140 ºC to 180 ºC. This may be due to the formation of the humins through the aldol reaction or the oligomerization of furfural. The selectivity and yield of furfural in different alcohol solvents are related to the nature of the solvent and the activity of the hydroxyl groups.[40a] The selectivity of furfural increased slightly then remained unchanged in MIBK with the increased temperature. This may be mainly due to the essential stability of MIBK. It is difficult to further react with furfural and can extract furfural to prevent its further conversion into humins.[40b] The maximum yield of 48% furfural was obtained at 160 ºC with 1-butanol as the organic phase. In particular, the highest product selectivity of 54% was achieved in 1-butanol at 160 ºC.

It has been reported that the halogen ions play an important role in the dehydration of carbohydrates to furans.[41] In order to investigate the effect of the halogen ions in the water-organic solvent biphasic system, NaCl (10 wt% in water) was added to the aqueous solution with six different solvents at 160 ºC (Fig. 1D). Unfortunately, yields of furfural slightly decreased in MTBE and MIBC, and no significant changes of furfural yields were observed in the other four solvents. These results demonstrated that the chloride ion had no obvious positive effect on the dehydration D-xylose to furfural in our reaction system. A possible reason was that ion exchange of NaCl with TA-p led to the slight decrease of reaction activity. To prove this hypothesis, TA-p was collected and dried after reaction and the BET surface areas and NH3-TPD studies of the catalyst TA-p were carried out (Supplemental Table. S1). Compared with TA-p without the adding of NaCl, the BET surface area and acid density of TA-p with the adding of NaCl had a slight decrease, proving the above explanation partially. Taking into account the above experimental results, 1-butanol was selected as the organic phase in this process for further study. Furthermore, 1-butanol was one of biomass-based alcohols, which could be prepared by the fermentation of biomass-based carbohydrates.[29c, 30a]

The effect of the reaction time on D-xylose dehydration was also studied at 160 oC using 1-butanol as the organic phase (Fig. 2A). The conversion of D-xylose increased along with the reaction time from 1 h to 10 h. D-xylose was almost completely converted after reacting for 5 h. However, the yield and selectivity of furfural firstly increased and then decreased slightly. The highest yield of 48% and the highest selectivity of 54% furfural were achieved at 3 h. It was possible that the reduced yield of furfural was attributed to the degradation of furfural in the reaction conditions. In order to verify the speculation, the degradation experiments of furfural were conducted. Furfural and TA-p were added to water and 1-butanol and stirred at 160 oC for a different period of time. The recoveries of furfural were determined from 1 h to 9 h. As shown in Fig. 2B, the furfural recoveries declined gradually with the extension of reaction time (from 86% to 49% with 1 h to 9 h), indicating the

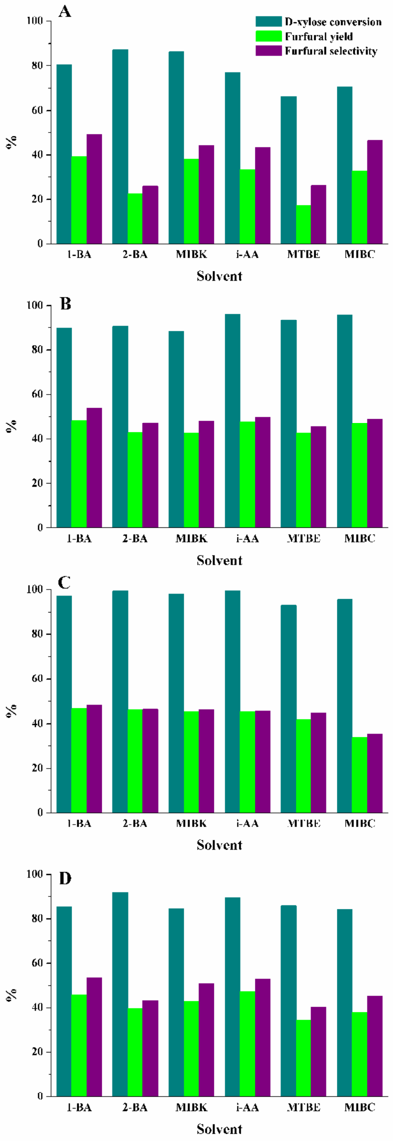

Fig. 1. Effect of reaction temperature and the adding of NaCl on the conversion of D-xylose to furfural in six different organic solvents: 140 ºC; B. 160 ºC; C. 180 ºC; D. Adding NaCl at 160 ºC. 1-butanol (1-BA), 2-butanol (2-BA), methyl isobutyl ketone (MIBK), iso-amyl alcohol (i-AA), methyl tert-butyl ether (MTBE) and methyl isobutyl carbinol (MIB ). Reaction conditions: 0.4 g of D-xylose, 400 mg of catalyst, 4 mL of water and 6 mL of organic solvent, 3 h.

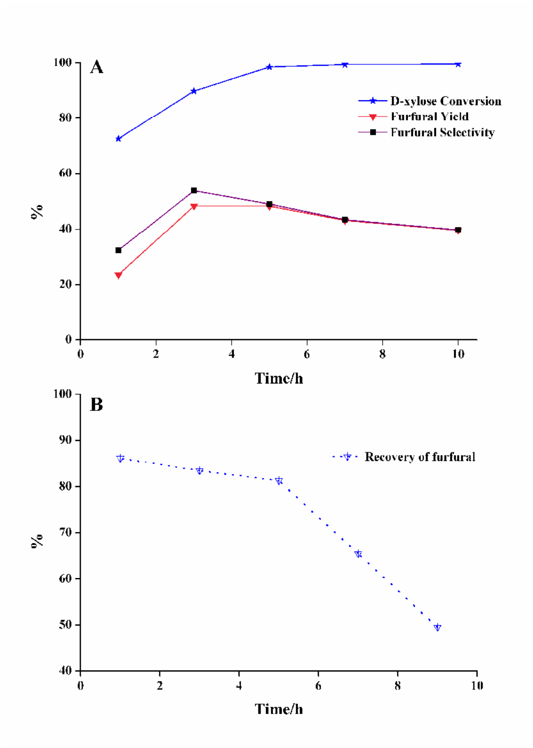

Fig. 2. Effect of reaction time on the conversion of D-xylose to furfural (A) and degradation experiments of furfural (B). Reaction condition: A: 0.4 g of D-xylose, 400 mg of catalyst, 4 mL of water and 6 mL of 1-butanol, 160 ºC; B: 0.256 g of furfural, 400 mg of catalyst, 4 mL of water and 6 mL of 1-butanol, 160 ºC.

gradual degradation of furfural in the reaction system with the extension of time. It was considered that long reaction time was not conducive to the reaction.

From the above the experimental results of the batch process, it could be seen that TA-p had a significant catalytic effect on the conversion of D-xylose to furfural. The highest furfural yield of 48% and the highest selectivity of 54% were achieved at 160 ºC in water-1-butanol biphasic system. Long reaction time would result in the degradation of furfural in the reaction conditions. A slight negative effect of chloride ion on TA-p was found in the reaction system. Above all, 1-butanol was selected as the organic phase in the continuous process for further study.

## 3.3. Continuous process of D-xylose conversion to furfural

For the purpose of improving the reaction efficiency, the fixed-bed reactor of a biphasic system was designed to convert D-xylose to furfural. As shown in the batch process, the reaction temperature was an important parameter. Therefore, the effect of the reaction temperature on the conversion of D-xylose into furfural was firstly investigated in the continuous process. LHSV was set at 1 $h^{-1}$ and the ratio of the aqueous phase to the organic phase was 1:1. The range of temperature was from 100 ºC to 220 ºC with the interval of 20 ºC. The system was filled with nitrogen to a pressure of 2.0 MPa. Unless special emphasis, the pressure 2 MPa was used. The results at different reaction temperature were shown in Fig. 3A. It was obvious that the reaction temperature had a great influence on the reaction. From 100 ºC to 220 ºC, the conversion of D-xylose was increased by 90% (from 8% to 98%). When the reaction temperature exceeded 180 ºC, D-xylose was almost completely converted. On the other hand, the yield of furfural showed a gradual upward trend first and then a slight downward trend with the increasing temperature. When the reaction temperature was below 160 ºC, the yield of furfural was not high due to the low conversion of D-xylose. The highest yield of 56% and the highest selectivity of 62% furfural were obtained at 180 ºC. D-xylose was nearly completely dehydrated with further increasing the reaction temperature, but the yield of furfural began to decrease presumably due to the degradation of furfural at the higher temperature. Therefore, the temperature of 180 ºC was selected as the appropriate reaction temperature for the following study.

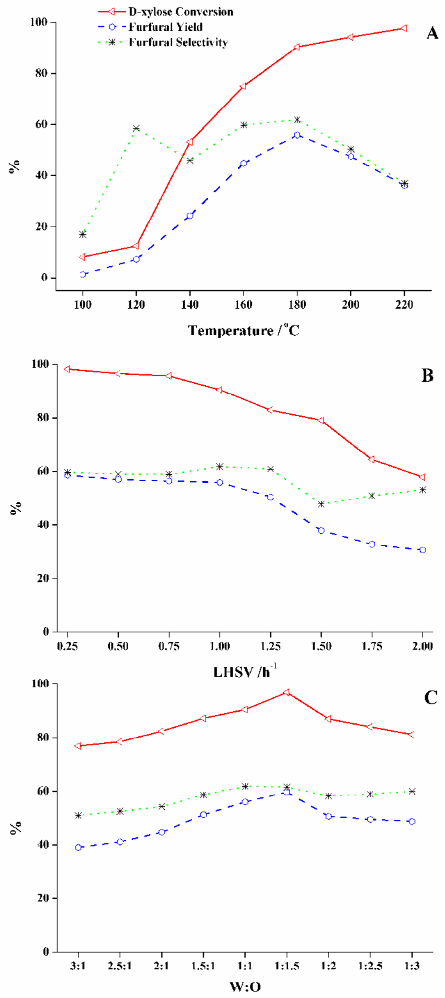

Fig. 3. Effect of reaction temperature (A), LHSV (B) and the ratio of the aqueous phase to 1-butanol (C) on the conversion of D-xylose to furfural in the fixed-bed catalytic system.

It was well known that LHSV was one of the most important parameters in the continuous process. Setting the reaction temperature at 180 oC and the ratio of the aqueous phase to

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DOI: 10.1039/C5RA11411J

organic phase was 1:1, LHSV varied from 0.25 $h^{-1}$ to 2 $h^{-1}$ with the interval of 0.25 $h^{-1}$, and the results were shown in Fig. 3B. The conversion of D-xylose and the yield of furfural decreased gradually with the increase of LHSV from 0.25 h-1 to 2.0 $h^{-1}$ in the process, indicating that LHSV had a significant effect on the reaction process. When LHSV was less than 1 $h^{-1}$, the conversion of D-xylose was more than 90% and yield of furfural was more than 55%. With the increase of LHSV from 1 $h^{-1}$ to 2.0 $h^{-1}$, the conversion of D-xylose and the yield of furfural decreased significantly due to the reduce of the contact time of the reaction mixture on the catalyst surface. It was noteworthy that lower LHSV could achieve higher conversion of D-xylose and furfural yield, but would shortenthe life of catalyst and lower production efficiency. Thus, LHSV of 1 $h^{-1}$ was selected for further research.

The ratio of the aqueous phase to the organic phase (W/O) was also a key factor to the continuous process. Setting the reaction temperature at 180 ºC and maintaining a constant feeding rate of the D-xylose aqueous solution at LHSV of 0.5 $h^{-1}$ (LHSV here means the volume of aqueous solution pumped into the fixed bed per hour / the volume of the catalyst loaded in the reactor), the feeding rate of organic solvent was changed to adjust the ratio of the aqueous phase to the organic phase from 3:1 to 1:3 (Fig. 3C). The results indicated that the ratio had an effect on the conversion of D-xylose (from 97% to 77%) and the yield of furfural (from 59% to 39%). Additionally, high content of water had a negative effect on the selectivity of furfural. On the contrary, the selectivity of furfural was almost constant with the ratio of the aqueous phase to the organic phase from 1:1 to 1:3. The highest D-xylose conversion of 96% and the highest furfural yield of 59% were obtained at the ratio of 1:1.5 (the aqueous phase: the organic phase). It was notable that high ratio of the organic phase to the aqueous phase in the process was not conducive to the conversion of D-xylose.

Summing up the above continuous processes, the optimized parameters were established. The highest D-xylose conversion of 96% and the highest furfural yield of 59% were achieved at 180 ºC, LHSV of 1 h-1 and the solvent ratio of 1:1.5 (the aqueous phase: the organic phase).

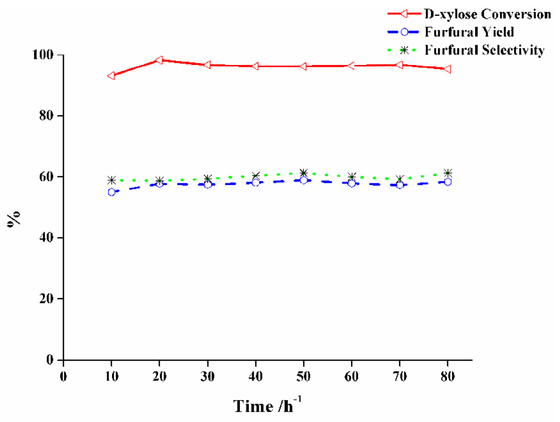

Fig. 4. The time-on-stream test under the optimal reaction conditions in the fixed-bed catalytic system.

Finally, in order to investigate the stability of the catalyst in the continuous system, the time-on-stream test was performed at the optimal reaction conditions (Fig. 4). After running for 80 h, the conversion of D-xylose remained almost unchanged (>95%) and the yield of furfural floated slightly (from 55% to 59%). This is indicated that a good stability of the TA-p catalyst in the continuous reaction system.

## 4. Conclusion

In summary, a water-tolerant and stable solid acid TA-p catalyst was developed for the dehydration of D-xylose to furfural in water-organic solvent biphasic system. In the batch process, 1-butanol was selected as the organic solvent and the highest furfural yield of 48% with the highest selectivity of 54% were achieved. In the continuous process, temperature, LHSV and the ratio of the aqueous phase to 1-butanol had an apparent effect on the conversion. The highest D-xylose conversion of 96% and the highest furfural yield of 59% were obtained. The long-time stability test for 80 h showed that TA-p catalyst had excellent stability.

## Acknowledgements

We gratefully acknowledge financial support from the National Natural Science Foundation of China (Nos. 21472033, 21402036 and 21272050), CPSF (2014M551793) and the Program for New Century Excellent Talents in University of the Chinese Ministry of Education (NCET-11-0627).

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