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# Direct synthesis of 2,5-diformylfuran from carbohydrates via carbonizing polyoxometalate based mesoporous poly(ionic liquid)

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# ABSTRACT

A promising atom-effective heterogeneous catalyst derived from the partial carbonization of polyoxometalate based mesoporous poly(ionic liquid) was constructed for the direct (one-pot and one-step) conversion of carbohydrates into 2,5-diformylfuran (DFF). The carbon precursor was synthesized through the free radical copolymerization of carboxylic acid functional ionic liquid and divinyl benzene, followed by the ion-exchange with heteropolyacid  $H_5PMo_{10}V_2O_{40}$  to introduce heteropolyanions. Partial carbonization dramatically enhanced the acid and oxidation properties, rendering the greatly strengthened activity in both the degradation of fructose into 5-hydroxymethylfurfural (HMF) and oxidation of HMF into DFF. As a result, the catalyst exhibited remarkable performance in the direct synthesis of DFF from fructose in a one-pot and one-step reaction, offering a high yield of 87.3% and a maximum turnover number (TON) of 77.7. The catalyst was facilely recovered and reused without apparent deactivation. The one-pot and one-step conversion of glucose into DFF reached the highest yield of 51.2% so far. Other carbohydrates such as inulin and sucrose were also effectively transformed into DFF, displaying good substrate compatibility.

# 1. Introduction

Developing green renewable resources has become growing significantly to alleviate the rapid depletion of fossil resources [1,2]. Biomass is one of the most important ones and exhibits to be the unique carbon-containing sustainable one [3–8]. Great efforts have been proposed for the transformation of these bio-resources into high valueadded chemicals and biofuels [6–8]. However, establishment of effective catalytic system is still challengeable. This is exemplified by the direct synthesis of 2,5-diformylfuran (DFF) from carbohydrates. In this context, design of highly effective heterogeneous catalyst is extremely urgent.

DFF is among the most valuable biomass derived platform molecules and has many potential applications such as the monomer of furan polymers, pharmaceutical intermediates and antibacterial agent [9,10]. Direct synthesis of DFF from carbohydrates is more attractive than that from 5-Hydroxymethylfurfural (HMF) [11,12]. The advantages include the abundant available raw materials and simplified synthetic route [13,14]. This straightforward synthesis is a tandem reaction involving multi-steps. Therefore, an effective conversion requires the catalyst possessing multi-functional active sites to synergistically catalyze the tandem reaction [15–17]. The employment of two or more catalysts is a simple way to allow multi-functions. For example, the combination of an acidic and an oxidative catalyst was used in the conversion of fructose into DFF. Alternatively, catalysts with both acid and oxidative sites were built to fulfill this requirement [18]. However, the activity of these catalysts in tandem reaction was normally inferior to the one in the oxidation of HMF into DFF [19-22]. In many cases, two-step reaction was used to alleviate the interference of the acid and oxidative sites, though the one-step is more favorable due to the facile operation [23–26]. Moreover, excessive catalyst or long reaction time was usually involved in these conversions, causing unsatisfied atom-efficiency with low turnover number (TON) and turnover frequency (TOF) [27-30]. Particularly, these drawbacks are aggravated in the conversion of the carbohydrates with more complicated structures (e.g. glucose), which combines several steps such as isomerization, dehydration, and selective oxidation [21-32]. Construction of effective catalyst is still on the way for the synthesis of DFF from carbohydrates, especially in a one-pot and one-step reaction.

In this work, we reported a fascinating strategy to design highperformance, single component heterogeneous catalyst for the one-pot and one-step conversion of various carbohydrates into DFF. Catalyst preparation relied on the partial carbonization of polyoxometalate (POM) based mesoporous poly(ionic liquid)s (MPILs). POMs are

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internal multi-functional catalysts with acid/base and redox properties [33,34]. Normally, they are dissolvable in polar solvents and heterogenization is achieved through immobilization or solidification [35,36]. MPILs characteristics of ionic liquid (IL) moieties in the polymeric framework are attractive catalysts and catalyst support, due to the existence of readily available multi-functional groups and IL-derived ionexchange properties [37-40]. The combination of POM and MPIL delivers a multitude of heterogeneous catalysts with facilely adjustable multi-functions [41]. MPILs have been used as favorable precursors towards high-performance carbon materials in many oxidation reactions [42,43]. However, to the best of our knowledge, there are no examples of the studies related to the carbonization of POM-based MPIL. Herein, we illustrated that partial carbonization enhanced the acidity and oxidative properties of carboxylic acid functional MPIL with  $PMo_{10}V_2O_{40}^{5-}$  (PMoV<sub>2</sub>) anions. The target catalyst was highly active in the direct synthesis of DFF from various carbohydrates (fructose, glucose, inulin and sucrose). High yield and TON were achieved in a onepot and one-step reaction, rendering a highly atom-efficient heterogeneous catalyst for this tandem transformation.

### 2. Experimental section

# 2.1. Reagents and materials

All of the following chemicals were commercially available and used without further treatment: 1-vinylimidazole (Aladdin Industrial Inc., 99%), 3-bromopropionic acid (Sinopharm Chemical Reagent Co., Ltd., 98%), diethenylbenzene (Aladdin Industrial Inc., 80%), phosphoric acid (Sigma-Aldrich,  $\geq$ 85%), vanadium pentoxide (Alfa Aesar, > 98%), HMF (Shanghai shaoyuan company, > 98%) and carbohydrates (glucose, fructose, sucrose and inulin, Aladdin Industrial Inc., > 99%).

# 2.2. Catalyst characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were acquired on a Bruker DPX 500 spectrometer by using D<sub>2</sub>O as the solvent and TMS (tetramethylsilane) as the internal reference. Solid state <sup>13</sup>C NMR spectra were originally recorded in a Bruker AVANCE-III spectrometer. Attenuated total reflection-Fourier transform infrared spectra (ATR-FTIR) were recorded on an Agilent Cary 660 instrument ranging from 4000 to 800 cm<sup>-1</sup>. Xray diffraction analysis (XRD) patterns were collected on a Smart Lab diffractmeter from Rigaku equipped with a 9kW rotating anode Cu source (45 kV, 200 mA, 5–80°,  $0.2^{\circ}$  s<sup>-1</sup>). In situ XRD was collected with heating in the range of 25–600 °C (10 °C min<sup>-1</sup>) under nitrogen (N<sub>2</sub>) atmosphere. Elemental analyses (EA) were performed with a CHN elemental analyzer Vario EL cube. Nitrogen sorption experiments were carried out at 77 K on a BELSORP-MAX analyser. The samples were degassed at 80 °C for 3 h before analysis. Scanning electron microscopic (SEM) images were viewed on a Hitachi S-4800 field-emission scanning electron microscope. Transmission electron microscopy (TEM) analysis was carried out on a JEM-2100 (JEOL) electron microscope (200 kV). Xray photoelectron spectra (XPS) was conducted on a PHI 5000 Versa Probe X-ray photoelectron spectrometer equipped with Al Karadiation (1486.6 eV). Thermogravimetric (TG) analysis in dry N<sub>2</sub> atmosphere proceeded on an STA409 instrument with the heating rate of 10 °C min<sup>-1</sup>. Inductively coupled plasma mass spectrometry (ICP) was measured at OPTMA 20,000 V. Temperature-programmed desorption (TPD) was analyzed by using Catalyst Analyzer BELCAT-B. Samples were pretreated at 300 °C for 60 min, and then cooled to 100 °C under helium (He) gas. NH3 adsorption was carried out at 100 °C for 60 min under a NH<sub>3</sub>/He (5% NH<sub>3</sub> and 95% He) gas. After samples were purged under He gas for 40 min, the temperature was heated to 300 °C (10 °C  $min^{-1}$ ). The desorbed gas was determined by a thermal conductivity detector (TCD).

## 2.3. Materials synthesis

Carboxylic acid functional IL [1-vinyl-3-propane carboxylation imidazolium]Br (VPI-Br) was solvothermally synthesized [39]. Elemental analysis calcd: C, 38.86 wt%; N, 11.24 wt%; H, 4.42 wt%; found: C, 38.81 wt%; N, 11.24 wt%; H, 4.36 wt%. <sup>1</sup>H NMR (300 MHz,  $D_2O$ , TMS) (ppm) = 3.01 (t, 2H, -CH<sub>2</sub>), 4.72 (t, 2H,-CH<sub>2</sub>), 5.45 (m, 1H, -CH), 5.81 (m, 1H, -CH), 7.17 (m, 1H, -CH), 7.63 (s, 1H, -CH), 7.79 (s, 1H, -CH), 9.12 (s, 1H, -CH) (Fig. S1).

MPIL P(DVPI-Br) was synthesized through free radical copolymerization of divinyl benzene (DVB) and VPI-Br by using azobisisobutyronitrile (AIBN) as the initiator. Typically, DVB (0.716 g, 5.5 mmol), VPI-Br (1.236 g, 5 mmol) and AIBN (0.09 g, 0.55 mmol) were dissolved in a mixture solution of ethanol (5 mL), H<sub>2</sub>O (20 mL) and ethyl acetate (25 mL) under a N<sub>2</sub> atmosphere. The resulting mixture was stirred at 353 K for 24 h. The white precipitate was isolated by filtration, washed with ethanol and ultimately dried at 373 K for 24 h (86% yield). Elemental analysis: C, 62.7 wt.%, N, 6.7 wt.%, H, 5.6 wt.%.

POM-based MPIL was synthesized through the reaction of P(DVPI-Br) with  $H_5PMo_{10}V_2O_{40}$  ( $H_5PMoV_2$ ), in which the POM anions were loaded through an ion-exchange process and immobilized via ionicbonding interaction. In a typical synthesis, P(DVPI-Br) and an aqueous solution of  $H_5PMoV_2$  (1/x g of  $H_5PMoV_2$  in 20 mL  $H_2O$ ; 1/x presents the mass ratio for P(DVPI-Br) and  $H_5PMoV_2$ ) was stirred at room temperature for 24 h. After that, the faint yellow precipitate was collected by filtration, washed with water and dried at 75 °C in a vacuum drying oven for 12 h. The resulted samples were termed PMoV<sub>2</sub>@P-*x*. PMoV<sub>2</sub>@ P-*x* were carbonized at preset temperature for 1 h in N<sub>2</sub> atmosphere (10 °C min<sup>-1</sup>), affording the partially carbonized samples PMoV<sub>2</sub>@CP-*x-y* (*y* presents the carbonation temperature).

# 2.4. Catalytic tests

Syntheses of DFF from HMF, HMF from fructose and DFF from carbohydrates (fructose, glucose, sucrose and inulin) were carried out in a 25 mL glass tube by using the target gas (balloon) and catalyst. In a typical run for the conversion of glucose into DFF, glucose (1 mmol, 180 mg), catalyst (90 mg) and dimethyl sulfoxide (DMSO, 4 mL) were stirred in the glass tube equipped with an O<sub>2</sub> balloon. After the reaction at 135 °C for 3 h, isopropanol (0.05 g) was added as the internal standard. The products were analyzed by gas chromatograph (GC, Agilent 7890B) equipped with a flame ionization detector and a capillary column (HP-5, 30m × 0.25 mm × 0.32 µm). Reusability was investigated by in a three-run recycling test. After each run, the catalyst was separated by centrifugation, washed with water, dried at 100 °C for 12 h, and then calcined at 400 °C for 1 h before recharging into the next run.

### 3. Results and discussion

# 3.1. Catalysts preparation and characterizations

Scheme 1 shows the preparation procedure of the target catalysts  $PMoV_2@CP-x-y$ . The synthesis involves three steps of 1) free radical copolymerization of IL monomer (VPI-Br) and DVB, 2) immobilization of  $PMoV_2$  anions through ion-exchange, and 3) carbonization under  $N_2$  atmosphere. The loading amount of  $PMoV_2$  was facilely adjusted by varying the initial mass ratio of P(DVPI-Br) to  $H_5PMoV_2$ , and the carbonization degree depended on the temperature. Herein, we took the typical sample  $PMoV_2@CP-5.5-400$  as an example. This catalyst was prepared with the initial  $P(DVPI-Br)/PMoV_2$  mass ratio of 5.5. A moderate carbonization temperature of 400 °C endowed the partial carbonization and satisfactory preservation of  $PMoV_2$  anions. Full characterizations were conducted to reveal the structure of  $PMoV_2@CP-5.5-400$  plus the two precursors of P(DVPI-Br) and  $PMoV_2@P-5.5$ . Elemental analysis (Table S1) indicated that the N

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Scheme 1. Preparation of PMoV<sub>2</sub>@CP-5.5-400.

Table 1 Textural properties.

Samples	IL content (mmol $g^{-1}$ ) <sup>a</sup>	PMoV <sub>2</sub> (wt%) <sup>b</sup>	$S_{BET}$ $(m^2 g^{-1})^c$	Vp (cm <sup>3</sup> g <sup>-1</sup> ) <sup>d</sup>	Dp (nm) <sup>e</sup>
VPI-Br P(DVPI-Br) PMoV2@P-5.5 PMoV2@CP-5.5-400	4.05 2.39 2.03	- 0 14.3 20.0	- 272 179 164	- 0.20 0.22 0.14	- 3.7 4.5 3.5

<sup>a</sup> IL content in MPILs calculated via elemental analysis.

<sup>b</sup> Total PMoV<sub>2</sub> loading.

<sup>c</sup> BET surface area.

d Total pore volume.

<sup>e</sup> Average pore diameter.

content of P(DVPI-Br) was 6.7%. The monomer DVB has no N element; therefore these N atoms come from the IL moieties in the ionic framework. The corresponding IL content of P(DVPI-Br) was 2.39 mmol g<sup>-1</sup>. PMoV<sub>2</sub>@P-5.5 exhibited the lower IL content of 2.03 mmol g<sup>-1</sup> due to the loading of POM anions. The N content of PMoV<sub>2</sub>@CP-5.5-400 was 4.1%, lower than the one of PMoV<sub>2</sub>@P-5.5 due to the decomposition of IL moieties. ICP analysis indicated that the loading amount of PMoV<sub>2</sub> anions of PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400 was 14.3% and 20%, respectively (Table 1).

Fig. 1 displays the SEM images of P(DVPI-Br), PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400. The primary particles of P(DVPI-Br) were small spheres with the diameter of about hundreds of nanometers (Fig. 1A). The spherical particles were loosely packed to form irregular secondary particles in micrometers. PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400 demonstrated similar morphology to P(DVPI-Br) (Fig. 1B and C), suggesting the preservation of the morphology during the ion-exchange and calcination process. This phenomenon also implies a partial carbonization of PMoV<sub>2</sub>@P-5.5 towards PMoV<sub>2</sub>@CP-5.5-400. Elemental mapping images demonstrated a uniformly distribution of PMoV<sub>2</sub> sites over PMoV<sub>2</sub>@CP-5.5-400 (Fig. 1D). TEM image of PMoV<sub>2</sub>@CP-5.5-400 additionally reflected a highly dispersion of the PMoV<sub>2</sub> active sites and the existence of abundant mesopores (Fig. 1E and F).

Qualitative analysis of the porosity was investigated by the nitrogen sorption experiments (Fig. 2). The nitrogen sorption isotherm of P (DVPI-Br) was type IV with a distinctive H<sub>2</sub> type hysteresis loop, implying the presence of micropores and mesopores [44,45]. Similar nitrogen sorption isotherms were observed over PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400, suggesting that these pores were preserved in these two samples. Table 1 summarizes the corresponding textural properties. Brunauer–Emmett–Teller (BET) surface area and pore volume of P(DVPI-Br) was  $272 \text{ m}^2 \text{ g}^{-1}$  and 0.195 cm<sup>3</sup> g<sup>-1</sup>, respectively. PMoV<sub>2</sub>@P-5.5 has a slightly lower surface area of 179 m<sup>2</sup> g<sup>-1</sup> but larger pore volume of 0.22 cm<sup>3</sup> g<sup>-1</sup>. This variation comes from the occupation

of the micropores by PMoV<sub>2</sub> anions, accompanying with the formation of certain mesopores. PMoV<sub>2</sub>@CP-5.5-400 owned the surface area of  $164 \text{ m}^2 \text{ g}^{-1}$  and pore volume of  $0.144 \text{ cm}^3 \text{ g}^{-1}$ . This phenomenon indicates that the calcination caused the collapse of partial mesopores.

Fig. 3A depicts the XRD patterns of P(DVPI-Br), PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400. P(DVPI-Br) demonstrated a wide peak around  $2\theta$ values of 20-30°, indicating that it has an amorphous structure. PMoV<sub>2</sub> presented the typical diffraction peaks for the Keggin type crystal structure of POM anions at 20 values of 8-11°, 18-22°, 24-30°, and 33-40° (Fig. 3B) [46]. These characteristic peaks were not observed in the XRD pattern of PMoV<sub>2</sub>@P-5.5, implying that these PMoV<sub>2</sub> anions are highly dispersed on the polymeric skeleton. PMoV<sub>2</sub>@CP-5.5-400 showed the similar XRD pattern to PMoV<sub>2</sub>@P-5.5, excluding the aggregation of these PMoV<sub>2</sub> anions during the calcination process. In situ XRD patterns of H<sub>5</sub>PMoV<sub>2</sub> under N<sub>2</sub> atmosphere were collected from 25 to 600 °C (Fig. 3B). The result showed that the Keggin type crystal structure of  $H_5PMoV_2$  was kept until a high temperature of 450 °C, validating that the PMoV<sub>2</sub> anions remained in PMoV<sub>2</sub>@CP-5.5-400. As the temperature increased to 500 °C, the peaks at 9° became weaken, along with the observation of a new peak at 12°. Additional new peaks at 23°, 24°, 27° and 33° were more and more apparent with the increasing of the temperature. The emergence of these signals indicates the formation of MoOx and VOx phase [47,48].

Fig. 4A illustrates the FT-IR spectra of these samples. The spectrum of PMoV<sub>2</sub> showed four main characteristic peaks in the range of  $800-2000 \text{ cm}^{-1}$ , in which the peaks at 786, 872, 947 and  $1052 \text{ cm}^{-1}$ stand for P-Oa (central oxygen), M-Ob-M (corner-sharing oxygen; M: metal in heteropolyacids framework), M-Oc-M (edge-sharing oxygen), and M-Od (terminal oxygen), respectively [49,50]. P(DVPI-Br) has the same peaks as reported [39]. The peak at 1720  $\text{ cm}^{-1}$  is attributable to the C=O stretching vibration in the carboxyl group. The peaks at 1157, 1448 and 1576 cm<sup>-1</sup> for the C–N and C=N stretching vibration reflect the existence of imidazole ring [51]. Both of the signals for the PMoV<sub>2</sub> anions and polymeric framework were observable in the spectrum of  $PMoV_2@P-5.5$ , revealing the immobilization of the  $PMoV_2$  anions on the MPIL skeleton. The characteristic peaks for the PMoV<sub>2</sub> anions were still observed in the spectrum of PMoV<sub>2</sub>@CP-5.5-400, indicating that these PMoV<sub>2</sub> anions remained after calcination, in accordance with the in situ XRD patterns. However, PMoV2@CP-5.5-400 demonstrated much weakened IR peaks assignable to the IL moieties, suggesting that these IL moieties were partially decomposed during the calcination. Solid state <sup>13</sup>C NMR spectra of PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400 were collected to further illustrate the variation of the polymeric framework during the calcination (Fig. 4B). The spectrum of PMoV<sub>2</sub>@P-5.5 presented typical signals attributable to the MPIL network. The two peaks at 136 and 173 ppm came from the C3 and C8 in the IL moieties of PMoV<sub>2</sub>@P-5.5 [39]. Both of them disappeared in the spectrum of



Fig. 1. SEM images of (A) P(DVPI-Br), (B) PMoV<sub>2</sub>@P-5.5 and (C) PMoV<sub>2</sub>@CP-5.5-400; (D) elemental (Br, Mo and V) mapping images of PMoV<sub>2</sub>@CP-5.5-400; (E, F) TEM images of PMoV<sub>2</sub>@CP-5.5-400.

 $PMoV_2@CP-5.5-400$ , additionally reflecting the decomposition of IL moieties. The peak at 226 ppm emerged in the spectrum of  $PMoV_2@P-5.5$  was not observed in previous POM-free MPIL with the same organic framework. Thus, this signal is tentatively assigned to the C3 of the

 $PMoV_2$  tethered IL moieties, and the peak shift is attributable to the strong cation-anion interaction. This phenomenon is also suggestive of the partial decomposition of the IL moieties. In other words, the IL moieties interacting with  $PMoV_2$  were preserved in  $PMoV_2@CP-5.5$ -



**Fig. 2.** (A) N<sub>2</sub> sorption isotherms and (B) pore size distribution curves of P(DVPI-Br), PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400. The adsorption isotherms for samples PMoV<sub>2</sub>@P-5.5 and P(DVPI-Br) are shifted by 27 and 63 cm<sup>3</sup> g<sup>-1</sup>.



Fig. 3. XRD patterns of (A) P(DVPI-Br), PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400; (B) In situ XRD patterns of H<sub>5</sub>PMoV<sub>2</sub> under N<sub>2</sub> atmosphere.

400. Besides, signals derived from the C1, C2 C11 and C12 were still observable in the spectrum of  $PMoV_2@CP-5.5-400$ , evidencing that the remaining of DVB mediated polymeric framework [52].

Fig. 4C shows the TG curves of P(DVPI-Br) and PMoV<sub>2</sub>@CP-5.5-400. The weight loss below 150 °C comes from desorption of physical adsorbed water. P(DVPI-Br) started to decompose from 176 °C. The weight loss from 176 to 306 °C is assigned to the partial decomposition of IL moieties as the starting decomposition temperature of the DVB framework was normally higher than 300 °C [53]. The substantial weight loss from 306 to 430 °C includes the decomposition of DVB framework and IL moieties. The deep decomposition of the polymeric framework happened at high temperature (> 430 °C) and converted most of the organic compounds into N-doped carbon. In the TG curve of

PMoV<sub>2</sub>@CP-5.5-400, an apparent weight loss was observed from the same temperature (176 °C) as the one in the curve of P(DVPI-Br). Similar weight loss variation was found for PMoV<sub>2</sub>@CP-5.5-400, though with smaller weight loss in each stair than that for P(DVPI-Br). This phenomenon indicates that the IL moieties and DVB medicated framework were partially decomposed in the preparation of PMoV<sub>2</sub>@CP-5.5-400, ESR spectra of PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400 showed a clear enhancement of the signal for the formation of partly reduced V species (Fig. 4D) [54]. This result indicates that the carbonization process affects the electronic state of the PMoV<sub>2</sub> anions, causing the formation of partially reduced V(IV) species that were normally active in many oxidation reactions [55].

XPS analyses of PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400 were



**Fig. 4.** (A) FT-IR spectra of P(DVPI-Br), PMoV<sub>2</sub>@P-5.5, PMoV<sub>2</sub>@CP-5.5-400 and H<sub>5</sub>PMoV<sub>2</sub>; (B)  $^{13}$ C MAS NMR spectra of PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400; (C) TG curves of PMoV<sub>2</sub>@CP-5.5-400 and P(DVPI-Br); (D) ESR spectra of PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400.



Fig. 5. XPS analysis for (A) survey scan; (B) N 1s; (C) C 1s and (D) Mo 3d spectra of PMoV2@P-5.5 and PMoV2@CP-5.5-400.

performed to represent the electronic states of C, N and Mo (Fig. 5A). The signals of the V and P species were negligible due to the low loading amount. Two peaks at 398.3 and 401.3 eV were detected in the N 1 s XPS spectrum of PMoV<sub>2</sub>@P-5.5. They were related to the pyridinic N (-N=) and pyrrolic N ( $-N^+=$ ) in the imidazolinium rings (Fig. 5B) [56]. PMoV<sub>2</sub>@CP-5.5-400 also demonstrated two N 1 s XPS signals at 399.0 and 401.9 eV for the pyridinic and pyrrolic N [57], suggesting that part of the IL moieties remained in this sample. The variation of the peak location and intensity indicates that the  $-N^+$  species were preferentially decomposed relative to the -N=ones. The C 1 s XPS spectrum of PMoV<sub>2</sub>@P-5.5 (Fig. 5C) was fitted with three peaks at around 284.8, 286.4, and 288.7 eV, corresponding to C-C, C-O, and C=O/C=N, respectively [58]. The C-O signal of PMoV<sub>2</sub>@CP-5.5-400 slightly shifted to lower binding energy, due to the formation of carbon. PMoV<sub>2</sub>@P-5.5 represented the typical Mo 3d3/2 (235.4 eV) and 3d5/2 (232.2 eV) peaks for the  $Mo^{6+}$  species in PMoV<sub>2</sub> anions (Fig. 5D). The Mo XPS signal of PMoV<sub>2</sub>@CP-5.5-400 shifted to higher binding energy of 235.7 and 232.5 eV [57,59].

Heteropolyacids are traditional strong acids and their acidity is normally measured by Hamilton indicator. However, this method is only suitable for the white samples or the ones with only pale color. The partial carbonized samples are dark, and thus their acidity was characterized by NH<sub>3</sub>-TPD analysis. Desorption was stopped at 300 °C by considering that the organic component will be decomposed at high temperature (in such case, the desorption peak does not represent the NH<sub>3</sub> desorption). The desorption temperature of strong acid sites are normally higher than 400 °C, and NH<sub>3</sub>-TPD profiles in this work only reflect the variation of weak acid sites. As shown in Fig. 6, higher desorption temperature and larger peak area were observed over PMoV<sub>2</sub>@CP-5.5-400 relative to PMoV<sub>2</sub>@P-5.5. This phenomenon clearly illustrates that partial carbonization enhanced the acid strength and amount of weak acid sites. For comparison, NH<sub>3</sub>-TPD profiles of PMoV<sub>2</sub>@CP-5.5-500 and PMoV<sub>2</sub>@CP-5.5-600 were collected (Fig. S2).



Fig. 6. NH<sub>3</sub>-TPD curves of PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400.

The result indicates that carbonization at high temperature of 500 and 600 °C further increased the amount of weak acid sites, attributable to the formation of  $MO_x$  and  $VO_x$ . This phenomenon also suggests that majority of the strong acid sites were damaged due to the decomposition of POM anions at high temperature. Thus, partial carbonization at moderate temperature well maintains the strong acid sites and strengthens the weak acid sites.

# 3.2. Catalytic activities

 $PMoV_2@CP-5.5-400$  was employed as a heterogeneous catalyst in the synthesis of DFF from carbohydrates. P(DVPI-Br) and  $PMoV_2@P-5.5$ were parallel tested to gain insight into the structure-performance relationship. Their catalytic performance was studied in the oxidation of HMF into DFF, conversion of the typical carbohydrate fructose into HMF, and straightforward synthesis of DFF from various carbohydrates of fructose, glucose, inulin and sucrose.

The conversion of carbohydrates into DFF usually involves the

Table 2

Oxidation	of	HMF	into	DFF. <sup>a</sup>	
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Entry	Catalyst	Catalyst dosage (g)	$Y_{DFF}$ (%) <sup>b</sup>	TON <sup>c</sup>
1	None	-	0.4	-
2	P(DVPI-Br)	0.02	14.0	-
3	PMoV <sub>2</sub> @P-5.5	0.02	44.7	135.7
4	PMoV <sub>2</sub> @CP-5.5-400	0.02	51.2	111.2

<sup>a</sup> Reaction conditions: HMF 1 mmol, DMSO 4 mL, O<sub>2</sub> balloon, 120 °C, 3 h.

<sup>b</sup> The yield of DFF.

<sup>c</sup> TON = mol DFF/mol vanadium.

dehydration of carbohydrates into HMF and the successive oxidation of HMF into DFF [16]. The oxidation step is crucial for this reaction. Hence, we started the catalysis evaluation from the synthesis of DFF from HMF. As shown in Table 2, the DFF yield was below 1% in the absence of any catalyst. Owing to the lack of oxidative sites, P(DVPI-Br) offered a low DFF yield of 14.0%. The DFF yield increased to 44.7% by using PMoV<sub>2</sub>@P-5.5. PMoV<sub>2</sub>@CP-5.5-400 exhibited higher DFF yield of 51.2%, suggesting that partial carbonization strengthens the oxidation ability, which comes from the formation of more active V(IV) species. Actually, the corresponding activity depended on the loading amount of PMoV<sub>2</sub> anions and the carbonization degree. For example, we investigated the activity of several control catalysts with different PMoV<sub>2</sub> content and carbonization degree (Table S2), including PMoV<sub>2</sub>@CP-x-400 (x = 1.8, 2.7, 11) and PMoV<sub>2</sub>@CP-5.5-y (y = 500, 600). Yields over PMoV<sub>2</sub>@CP-1.8-400, PMoV<sub>2</sub>@CP-2.7-400 and PMoV<sub>2</sub>@CP-11-400 were 32%, 42.3% and 21.9%, respectively. PMoV<sub>2</sub>@CP-5.5-500 and PMoV<sub>2</sub>@CP-5.5-600 afforded the DFF yields of 33% and 19%. All of them are less active than PMoV<sub>2</sub>@CP-5.5-400, verifying that PMoV<sub>2</sub> content and carbonization degree played a vital role. The influence of the reaction temperature and catalyst dosage was surveyed in the PMoV<sub>2</sub>@CP-5.5-400 catalyzed oxidation of HMF into DFF (Fig. 7). Highest DFF yield of 90.4% (TON: 98.1) was obtained by using 0.04 g catalyst at 130 °C. Maximum DFF TON of 113 was reached by slightly reducing the catalyst dosage to 0.03 g. Compared with previous work (Table S3), the activity of PMoV<sub>2</sub>@CP-5.5-400 was superior to or at least comparable to the best ones. Particularly, TON value over PMoV<sub>2</sub>@CP-5.5-400 was among the highest ones under similar reaction conditions [60,61].

Table 3 demonstrates the performance of P(DVPI-Br), PMoV<sub>2</sub>@P-5.5 and PMoV<sub>2</sub>@CP-5.5-400 in the one-pot and one-step synthesis of DFF from the typical carbohydrate fructose. Catalyst-free reaction rendered a low DFF yield of 4.2%. P(DVPI-Br) exhibited improved activity in the conversion of fructose into HMF, but was inactive in the oxidation step. Thus, P(DVPI-Br) catalyzed reaction afforded a high HMF yield of 60.2% with a low DFF yield of 9.6%. PMoV<sub>2</sub>@P-5.5 exhibited slightly enhanced activity, offering the DFF yield of 20.0%. Unexpectedly, PMoV<sub>2</sub>@CP-5.5-400 resulted in an effective conversion of fructose into Catalysis Today xxx (xxxx) xxx-xxx

 Table 3

 One-pot and one-step conversion of fructose into DFF.<sup>a</sup>

Entry	Catalyst	Catalyst dosage (g)	$Y_{HMF}$ (%) <sup>b</sup>	Y <sub>DFF</sub> (%) <sup>c</sup>	TON <sup>d</sup>
1	None	-	9.1	4.2	_
2	P(DVPI-Br)	0.04	60.2	9.6	-
3	PMoV <sub>2</sub> @P-5.5	0.04	50.5	20.0	30.3
4	PMoV <sub>2</sub> @CP-5.5-	0.04	0.6	71.6	77.7
	400				

<sup>a</sup> Reaction conditions: fructose 1 mmol, DMSO 4 mL, 130 °C, 3 h.

<sup>b</sup> The yield of HMF.

c The yield of DFF.

<sup>d</sup> TON = mol DFF/mol vanadium.

DFF with the yield of 71.6% under the same reaction conditions. The corresponding TON was as high as 77.7. Further altering of the reaction time and catalyst dosage leaded to a high DFF yield of 87.3% (TON: 47.4) (Fig. 8). Such activity in the one-pot and one-step reaction greatly exceeds previous heterogeneous catalysts under the identical reaction conditions (Table S3, yields: 39–69.3%; TONs: 3.4–12.3) [23,26,29]. Also, its performance is even superior to or comparable to the ones of the two-step reactions [32]. It is noted that the activity (yield and TON) of this catalyst in the conversion of fructose into DFF is close to the one in the oxidation of HMF into DFF. This interesting finding highlights that the acidic and oxidative sites in this catalyst were able to smoothly and independently catalyze each step (dehydration and oxidation), and thus synergistically catalyzed the conversion of fructose into DFF in a one-pot and one-step reaction. This is scarcely achieved before.

The kinetic curve indicates the accumulation of HMF in the initial stage of the reaction, while DFF was gradually produced along with the decrease of HMF. This proves that PMoV<sub>2</sub>@CP-5.5-400 catalyzed conversion of fructose into DFF underwent the formation of HMF (Fig. 8). The investigation of the PMoV<sub>2</sub> loading amount suggests that  $PMoV_2@CP-5.5-400$  was more active than  $PMoV_2@CP-x-400$  (x = 1.8, 2.7, 11) (Table S4), in agreement with their performance in the oxidation of HMF into DFF (Table S2). PMoV<sub>2</sub>@CP-5.5-400 was only slightly more active than PMoV<sub>2</sub>@P-5.5 in the oxidation step (yield: 51.2% vs 44.7%), but the former presented much higher yield than the latter in the conversion of fructose into DFF (yield: 71.6% vs 20.0%). In order to gain insightful understanding, we conducted the synthesis of HMF from fructose by using PMoV<sub>2</sub>@CP-5.5-400 and PMoV<sub>2</sub>@P-5.5 under N<sub>2</sub> atmosphere. Fructose was rapidly converted into HMF when catalyzed by PMoV<sub>2</sub>@CP-5.5-400, affording the yield of 59.6% within 0.5 h. A high yield of 88.2% was achieved at 1 h. It is intensely higher than that over PMoV<sub>2</sub>@P-5.5 (Fig. 9, yield: 75.2%). This phenomenon clearly reveals that partial carbonization of PMoV<sub>2</sub>@P-5.5 strengthens both the acidity and oxidative ability that drives the efficient synergistic catalysis in this tandem reaction. After reaction, the catalyst PMoV<sub>2</sub>@CP-5.5-400 was facilely recovered and reused without significant deactivation (Fig. S3). PMoV<sub>2</sub> content in the spent catalyst was



Fig. 7. Influence of reaction temperature and catalyst dosage on the PMoV<sub>2</sub>@CP-5.5-400 catalyzed conversion of HMF to DFF. Reaction conditions: HMF 1 mmol, catalyst 0.03 g, DMSO 4 mL, 3 h, 130 °C, 3 h O<sub>2</sub> balloon. For each figure there is a specific parameter changed.



Fig. 8. Influence of (A) reaction time and (B) catalyst amount on the PMoV<sub>2</sub>@CP-5.5-400 catalyzed one-pot and one-step conversion of fructose into DFF. Reaction conditions: fructose 1 mmol, DMSO 4 mL, O<sub>2</sub> balloon; (A) 120 °C, catalyst 0.08 g; (B) 110 °C, 4 h. For each figure there is a specific parameter changed.



Fig. 9. Yields as a function of reaction time in the  $PMoV_2@CP-5.5-400$  catalyzed conversion of fructose into HMF. Reaction conditions: fructose 1 mmol, DMSO 4 mL, 120 °C, catalyst 0.08 g,  $N_2$  balloon.

18.1% that is close to the one in the fresh catalyst (Table 1).

The scope of PMoV<sub>2</sub>@CP-5.5-400 was explored in the transformation of other carbohydrates into DFF. The conversion of glucose into DFF involves three steps (Table 4), and thus is much more difficult than the transformation of fructose. Exhilaratingly,  $PMoV_2$ @CP-5.5-400 afforded a high DFF yield of 46.3% in the one-pot and one-step synthesis of DFF from glucose. This activity was about 2.6-fold of the one over  $PMoV_2$ @P-5.5 (17.6%), reflecting an apparent enhanced activity derived from the partial carbonization. Kinetic analysis also demonstrated the conversion of glucose into DFF via HMF (Fig. 10). As

#### Table 4

One-pot and one-step con	version of different	carbohydrates i	into DFF. <sup>*</sup>
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Entry	Substrate	Catalyst	PMoV <sub>2</sub> (wt %) <sup>b</sup>	Y <sub>HMF</sub> (%) <sup>c</sup>	Y <sub>DFF</sub> (%) <sup>d</sup>	TON <sup>e</sup>
1 2	glucose glucose	PMoV2@P-5.5 PMoV2@CP-5- 400	14.3 21.9	3.4 1.9	17.6 40.7	11.9 17.9
3	glucose	PMoV <sub>2</sub> @CP-5.5- 400	20	1.2	46.3	22.3
4	glucose	PMoV <sub>2</sub> @CP-6- 400	16.7	0.4	51.2	29.6
5	inulin	PMoV <sub>2</sub> @CP-5.5- 400	20	0.6	61.6	29.7
6	sucrose	PMoV <sub>2</sub> @CP-5.5- 400	20	0.2	20.4	9.8

 $^{\rm a}$  Reaction conditions: carbohydrates 1 mmol, DMSO 4 mL, catalyst 0.09 g, 135 °C, 5 h.

<sup>b</sup> Total PMoV<sub>2</sub> loading.

<sup>c</sup> The yield of HMF.

<sup>d</sup> The yield of DFF.

<sup>e</sup> TON = mol DFF/mol vanadium.



**Fig. 10.** Yields as a function of reaction time in the  $PMoV_2@CP-5.5-400$  catalyzed conversion of glucose into DFF. Reaction conditions: glucose 1 mmol, DMSO 4 mL, 135 °C, catalyst 0.09 g, O<sub>2</sub> balloon.

aforementioned, the loading amount of  $PMoV_2$  significantly affected the performance. Finely manipulation of the  $PMoV_2$  content led to additionally increased activity by using  $PMoV_2@CP-6-400$  (yield: 51.2%). The resulting activity is among the highest ones even compared with those of two-step reactions (Table S3) [18,32]. Also much high TON (29.6) was reached compared with previous results (Table S3, TONs: 1.6–15). Further, inulin and sucrose were effectively converted into DFF in this straightforward transformation process, rendering the DFF yields of 61.6% and 20.4% (Table 4), respectively. All of these emphasize the good substrate compatibility of this catalyst.

The above catalysis evaluation indicates that partial carbonization of POM-based MPIL provided highly active heterogeneous catalyst in the direct synthesis of DFF from carbohydrates. Partial carbonization is crucial for such good performance. Structure analysis by ESR (Fig. 4D) and XPS (Fig. 5) spectra demonstrated that partial carbonization caused the formation of more positive Mo species and more negative V species, suggesting the electron transfer from Mo to V. Normally, the V species are the oxidative sites in an oxidation reaction and partial reduced V species responded higher activity in many cases [54,62]. NH<sub>3</sub>-TPD test implied that the weak acid sites were strengthened and strong acid sites were well preserved after partial carbonization (Figs. 6 and S2). Direct synthesis of DFF from carbohydrates is a tandem reaction involving an acid-catalyzed conversion of carbohydrate into HMF and successive oxidation of HMF into DFF. The enhanced oxidative ability promoted the activity in the oxidation step (Table 2), while the variation of the acidity increased the activity in the acid-hydrolysis step (Fig. 9). Owing to these two enhancements, the obtained catalyst after partial carbonization represented high activity in this tandem reaction. High carbonization temperature caused low surface area (Fig. S4 and Table S5) and the formation of  $MoO_x$  and  $VO_x$  (Fig. 3B). By contrast, carbonization at moderate temperature tended to preserve the high surface area

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and structure of POM anions, which also contributes to the high performance.

# 4. Conclusions

Partial carbonization of  $PMoV_2$  based MPIL promoted the acid and oxidation catalysis capability. The target catalyst  $PMoV_2@CP-5.5-400$ exhibited the remarkable performance in the one-pot and one-step conversion of the carbohydrates (fructose, glucose, inulin and sucrose) into DFF. This transformation featured the high yields and excellent TONs, and thus is a highly efficient process. The result offered a new kind of promising heterogeneous catalyst for the biomass conversion by providing multi-functional catalytic active sites.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2018.07.042.

## References

- [1] P. Zhou, Z.H. Zhang, Catal. Sci. Technol. 6 (2016) 3694–3712.
- [2] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411–2502.
- [3] B. Donoeva, N. Masoud, P.E. Jongh, ACS Catal. 7 (2017) 4581-459.
- [4] N. Yan, X. Chen, Nature 524 (2015) 155–157.
- [5] B. Xiang, Y. Wang, T. Qi, H.Q. Yang, C.W. Hu, J. Catal. 352 (2017) 586–598.
- [6] X.Y. Wan, C.M. Zhou, J.S. Chen, W.P. Deng, Q.H. Zhang, Y.H. Yang, Y. Wang, ACS Catal. 4 (2014) 2175–2185.
- [7] S. Xu, P. Zhou, Z.H. Zhang, C.J. Yang, B.G. Zhang, K.J. Deng, S. Bottle, H.Y. Zhu, J. Am. Chem. Soc. 139 (2017) 14775–14782.
- [8] X. Chen, H.Y. Yang, Z.Y. Zhong, N. Yan, Green Chem. 19 (2017) 2783–2792.
- [9] G.Q. Lv, H.L. Wang, Y.X. Yang, T.S. Deng, C.M. Chen, Y.L. Zhu, X.L. Hou, ACS Catal. 5 (2015) 5636–5646.
- [10] G. Yadav, R. Sharma, Appl. Catal. B: Environ. 147 (2014) 293–301.
- [11] C.T. Chen, C.V. Nguyen, Z.Y. Wang, Y. Bando, Y. Yamauchi, M.T.S. Bazziz, A. Fatehmulla, W.A. Farooq, T. Yoshikawa, T. Masuda, K.C.W. Wu, ChemCatChem 10 (2018) 361–365.
- [12] M. Chatterjee, T. Ishizaka, A. Chatterjee, H. Kawanami, Green Chem. 19 (2017) 1315–1326.
- [13] Z.Z. Yang, W. Qi, R.X. Su, Z.M. He, ACS Sustain. Chem. Eng. 5 (2017) 4179-4187.
- [14] R.Q. Fang, R. Luque, Y.W. Li, Green Chem. 19 (2017) 647–655.
- [15] Y. Liu, L.F. Zhu, J.Q. Tang, M.Y. Liu, R. Cheng, C.W. Hu, ChemSusChem 7 (2014) 3541–3547.
- [16] J.J. Wang, W.J. Xu, J.W. Ren, X.H. Liu, G.Z. Lu, Y.Q. Wang, Green Chem. 13 (2011) 2678–2681.
- [17] G.A. Halliday, R.J. Young, V.V. Grushin, Org. Lett. 5 (2003) 2003–2005.
- [18] A. Takagaki, M. Takahashi, S. Nishimura, K. Ebitani, ACS Catal. 1 (2011)
- 1562–1565.
- [19] Z.Z. Yang, J. Deng, T. Pan, Q.X. Guo, Y. Fu, Green Chem. 14 (2012) 2986–2989.
   [20] C. Laugel, B. Estrine, J.L. Bras, N. Hoffmann, S. Marinkovic, J. Muzart, ChemCatChem 6 (2014) 1195–1198.

- [21] W. Ghezali, K.D.O. Vigier, R. Kessasb, F. Jerome, Green Chem. 17 (2015) 4459–4464.
- [22] W. Zhang, J.Y. Xie, W. Hou, Y.Q. Liu, Y. Zhou, J. Wang, ACS Appl. Mater. Interfaces 8 (2016) 23122–23132.
- [23] J. Chen, Y. Guo, J. Chen, L. Song, L. Chen, ChemCatChem 6 (2014) 3174–3181.
   [24] R.L. Liu, J.Z. Chen, X. Huang, L.M. Chen, L.L. Ma, X.J. Li, Green Chem. 15 (2013)
- 2895–2903. [25] Z. Zhang, Z. Yuan, D. Tang, Y. Ren, K. Lv, B. Liu, ChemSusChem 7 (2014)
- 3496–3504.
- [26] R. Liu, J. Chen, L. Chen, Y. Guo, J. Zhong, ChemPlusChem 79 (2014) 1448–1454.
- [27] R.Q. Fang, R. Luque, Y.W. Li, Green Chem. 18 (2016) 3152–3157.
   [28] X.X. Liu, J.F. Xiao, H. Ding, W.Z. Zhong, Q. Xu, S.P. Su, D.L. Yin, Chem. Eng. J. 283 (2016) 1315–1321.
- [29] W. Zhang, T.S. Meng, J.J. Tang, W.X. Zhuang, Y. Zhou, J. Wang, ACS Sustain. Chem. Eng. 5 (2017) 10029–10037.
- [30] K.M. Eblagon, M.F.R. Pereira, J.L. Figueiredo, Catal. Today 301 (2018) 55-64.
- [31] Q. Girka, N. Hausser, B. Estrine, N. Hoffmann, J.L. Bras, S. Marinkovicb, J. Muzarta, Green Chem. 19 (2017) 4074–4079.
- [32] P.V. Rathod, S.D. Nale, V.H. Jadhav, ACS Sustain. Chem. Eng. 5 (2017) 701-707.
- [33] P.P. Zhao, Y. Leng, J. Wang, Chem. Eng. J. 206 (2012) 72–78.
- [34] Z.Y. Long, Y. Zhou, W.L. Ge, G.J. Chen, J.Y. Xie, Q. Wang, J. Wang, ChemPlusChem 79 (2014) 159–1596.
- [35] V.M. Shinde, E. Skupien, M. Makkee, Catal. Sci. Technol. 5 (2015) 4144–4153.
   [36] H. Wang, K. Jiang, Q.L. Chen, Z.X. Xie, W.B. Cai, Chem. Commun. 52 (2016)
- [50] H. Wang, K. Jiang, Q.L. Chen, Z.A. Ale, W.B. Cai, Chem. Commun. 52 ( 374–377.
- [37] W.J. Qian, J. Texter, F. Yan, Chem. Soc. Rev. 46 (2017) 1124-1159.
- [38] D. Mecerreyes, Prog. Polym. Sci. 36 (2011) 1629–1648.
- [39] Q. Wang, X.C. Cai, Y.Q. Liu, J.Y. Xie, Y. Zhou, J. Wang, Appl. Catal. B: Environ. 189 (2016) 242–251.
- [40] P.F. Zhang, Z.A. Qiao, X.G. Jiang, G.M. Veith, S. Dai, Nano Lett. 15 (2015) 823–828.
   [41] G.J. Chen, W. Hou, J. Li, X.C. Wang, Y. Zhou, J. Wang, Dalton Trans. 45 (2016)
- 4504–4508. [42] Yan Leng, Jun Wang, Dunru Zhu, Xiaogian Ren, Hanging Ge, Lei Shen, Angew.
- Chem. Int. Ed. 48 (2009) 168–171. [43] X.C. Cai, Q. Wang, Y.Q. Liu, J.Y. Xie, Z.Y. Long, Y. Zhou, J. Wang, ACS Sustain.
- Chem. Eng. 4 (2016) 4986–4996.
- [44] Z.X. Xu, X.D. Zhuang, C.Q. Yang, J. Cao, Z.Q. Yao, Y.P. Tang, J.Z. Jiang, D.Q. Wu, X.L. Feng, Adv. Mater. 28 (2016) 1981–1987.
- [45] Z.B. Zhang, Q. Zhao, J.Y. Yuan, M. Antonietti, F.H. Huang, Chem. Commun. 50 (2014) 2595–2597.
- [46] H.F. Wang, L.P. Fang, Y.F. Yang, L. Zhang, Y.J. Wang, Catal. Sci. Technol. 6 (2016) 8005–8015.
- [47] L. Kong, J.M. Li, Z. Zhao, Q.L. Liu, Q.Y. Sun, J. Liu, Y.C. Wei, Appl. Catal. A: Gen. 510 (2016) 84–97.
- [48] A. Zeb, X. Xie, A.B. Yousaf, M. Imran, T. Wen, Z. Wang, H.L. Guo, Y.F. Jiang, I.A. Qazi, A.W. Xu, ACS Appl. Mater. Interface 8 (2016) 30126–30132.
- [49] P.P. Zhao, J. Wang, G.J. Chen, Y. Zhou, J. Huang, Catal. Sci. Technol. 3 (2013) 1394–1404
- [50] B.B. Bardin, R.J. Davis, Appl. Catal. A: Gen. 185 (1999) 283–292.
- [51] X.C. Wang, Y. Zhou, Z.J. Guo, G.J. Chen, J. Li, Y.M. Shi, Y.Q. Liu, J. Wang, Chem. Sci. 6 (2015) 6916–6924.
- [52] X.C. Wang, J. Li, G.J. Chen, Z.J. Guo, Y. Zhou, J. Wang, ChemCatChem 7 (2015) 993–1003
- [53] Q. Wang, W. Hou, S. Li, J.Y. Xie, J. Li, Y. Zhou, J. Wang, Green Chem. 19 (2017) 3820–3830.
- [54] Z.Y. Long, Y. Zhou, G.J. Chen, W.L. Ge, J. Wang, Sci. Rep. 4 (2014) 3651–3655.
   [55] Z.Z. Yuan, Y.Q. Duan, H.Z. Zhang, X.F. Li, H.M. Zhang, I. Vankelecom, Energy
- Environ. Sci. 9 (2016) 441–447. [56] Y. Lin, X. Pan, W. Qi, B. Zhang, D.S. Su, J. Mater. Chem. A 2 (2014) 12475–12483.
- [57] Y. Li, B. Li, L. Geng, J. Wang, Y. Wang, J. Huang, Catal. Lett. 145 (2015) 1014–1021.
- [58] Y.P. Zang, H.M. Zhang, X. Zhang, R.R. Liu, S.W. Liu, G.Z. Wang, Y.X. Zhang, H.J. Zhao, Nano Res. 9 (2016) 2123–2137.
- [59] F.F. Ju, D. VanderVelde, E. Nikolla, ACS Catal. 4 (2014) 1358-1364.
- [60] F. Neaţu, N. Petrea, R. Petre, V. Somoghi, M. Florea, V.I. Parvulescu, Catal. Today 278 (2016) 66–73.
- [61] C.M. Sayago, C.J. Carrasco, S. Ivanova, F.J. Montilla, A. Galindo, J.A. Odriozola, Catal. Today 278 (2016) 82–90.
- [62] A.M. Khenkin, L. Weiner, Y. Wang, R. Neumann, J. Am. Chem. Soc. 123 (2001) 8531–8542.