

Catalysis Science & Technology

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: H. Wang, C. Wang, Y. Yang, M. Zhao and Y. Wang, *Catal. Sci. Technol.*, 2016, DOI: 10.1039/C6CY01669C.



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. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

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 ethical guidelines, outlined in our <u>author and reviewer resource centre</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.



rsc.li/catalysis

View Article Online View Journal

# CROYAL SOCIETY

# **Catalysis Science & Technology**

# PAPER

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/mpg-C<sub>3</sub>N<sub>4</sub> as efficient and reusable bifunctional catalyst in one-pot oxidation-Knoevenagel condensation tandem reaction

Hefang Wang, Cunyue Wang, Yongfang Yang\*, Meng Zhao, Yanji Wang\*

A single-site bifunctional catalyst for the oxidation-Knoevenagel condensation tandem reaction was prepared by the immobilization of phosphotungstic acid (HPW) on mesoporous graphitic carbon nitride (mpg- $C_3N_4$ ) via electrostatic interaction (HPW/mpg- $C_3N_4$ ). The results of Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), solid-state <sup>31</sup>P nuclear magnetic resonance (solid-state <sup>31</sup>P NMR), zeta potentials, X-ray photoelectron spectroscopy (XPS) and thermo gravimetric analysis (TGA) demonstrated that HPW was successfully immobilized on the protonated  $mpg-C_3N_4$  by electrostatic interaction. The acid amounts of the catalysts were determined by ammonia temperature programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD). The textural and morphology of HPW/mpg- $C_3N_4$  were characterized by N<sub>2</sub> adsorption-desorption, scanning electronic micrograph (SEM) and transmission electron microscope (TEM). 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> shows the best catalytic performance in the tandem reaction with 98.4% benzyl alcohol conversion and 96.2% selectivity to benzylidene malononitrile. The excellent catalytic performance of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> in the tandem reaction is due to the good catalytic performance of HPW in the oxidation and Knoevenagel condensation, respectively. Furthermore, protonated mpg- $C_3N_4$  not only acts as support to facilitate good dispersion of HPW but also promotes the Knoevenagel condensation reaction effectively. Moreover, the HPW/mpg-C<sub>3</sub>N<sub>4</sub> catalyst could be recycled easily without significant loss of catalytic activity.

# 1. Introduction

The Knoevenagel condensation of aldehydes with compounds containing activated methylene groups is a

facile and versatile route to the formation of carboncarbon bond with numerous applications in the synthesis of fine chemicals as well as heterocyclic compounds of biological significance.<sup>1,2</sup> Various catalysts, such as graphitic carbon nitride,<sup>3,4</sup> metal-organic framework (MIL-100(Al), UiO-66 and ZIF-8),<sup>5,6</sup> polyoxometalate intercalated layered double hydroxide composite materials,<sup>7</sup> amine functionalized K10 montmorillonite,<sup>8</sup> amine-functionalized mesoporous zirconia,<sup>9</sup> nanocrystall-

School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China

E-mail address: <u>wuyuyang123456@163.com</u> (Y. Yang), <u>yiwang@hebut.edu.cn</u> (Y. Wang)

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

ine  $Ce_xZr_{1-x}O_2$ ,<sup>10</sup> showed high catalytic activity towards Knoevenagel condensation reactions at mild conditions. In general, Knoevenagel condensation reactions are promoted not only by base catalysts but also by acid catalysts.<sup>10</sup> Among these catalysts, the acidic-base bifunctional catalysts, such as polyoxometalate intercalated layered double hydroxide composite materials,<sup>7</sup> amine functionalized K10 montmorillonite<sup>8</sup> and nanocrystalline  $Ce_xZr_{1-x}O_2^{10}$  were considerable attractive for their high catalytic efficiency. The synergistic effect between the acidic and basic sites is crucial in the catalytic process.

Tandem reactions, which enable multistep reactions in one pot, increase the economic competitiveness in the production of target compounds and the greenness of the whole process by reducing capital investment, being effective in the minimization of wastes and energy consumption and optimizing the use of solvents.<sup>11,12</sup> Thus one-pot synthesis of benzylidene malononitrile has raised extensive interest as an attractive synthetic concept for improving overall process efficiency.<sup>13,14</sup> Benzylidene malononitrile was reported to be obtained by tandem deacetalization-Knoevenagel condensation reaction or oxidation-Knoevenagel condensation reaction. Several acid-base bifunctional catalysts were used in one-pot deacetalization-Knoevenagel condensation reaction with good yields, which were reported by Shiju,<sup>15</sup> Zhong,<sup>16</sup> Lu,<sup>17</sup> Xu,<sup>18</sup> Goyal,<sup>19</sup> Gianotti<sup>1</sup> and Zhang<sup>20</sup>. However, the preparation of multifunctional catalysts with both acids and bases active sites is complicated, due to the incompatible nature of active sites.<sup>1</sup>

Recently, Zr-MOF-NH<sub>2</sub><sup>21</sup> and NH<sub>2</sub>-MIL-101(Fe)<sup>22</sup> were used for one-pot sequential photocatalytic aerobic oxidation-Knoevenagel condensation reaction by light irradiation. However, excess malononitrile was required in the reaction, owing to the decrease of reaction rate of Knoevenagel condensation under UV-light irradiation. Moreover, unstability is one of the major drawbacks of MOFs based catalysts.<sup>11,23</sup> Furthermore, aerobic oxidation-Knoevenagel condensation reaction has been also reported by a series of researchers including Qi,<sup>24</sup> Chen,<sup>25</sup> Ang,<sup>26</sup> Sarmah,<sup>27</sup> Horiuchi<sup>28</sup> and so on. During the aerobic oxidation reaction, noble metals were used as catalysts with molecular oxygen as oxidant.

More recently, Au/NH2-UiO-66 was used as catalyst in oxidation-Knoevenagel condensation reaction with tert-butyl hydroperoxide (TBHP) as oxidant, whereas noble metal Au and a long reaction time (34 h) were required.<sup>29</sup> Thus, it is urgent to design noble metal-free and more efficient catalyst to develop a green and mild one-pot oxidation-Knoevenagel condensation reaction system. The catalytic oxidation of alcohols with hydrogen peroxide as oxidant over heterogeneous catalyst has received considerable attention from the viewpoint of green chemistry.<sup>30,31</sup> Hydrogen peroxide as a green oxidant is attractive and competitive for oxidation reactions,<sup>32</sup> which can provide abundant active oxygen species with water as the only byproduct. Hydrogen peroxide is much cheaper and safer than organic peroxides and peracids.31,33,34

Polyoxometalates (POMs), especially phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, HPW), due to its controllable redox and acidic properties, have been used as effective catalysts in oxidation<sup>35,36</sup> and Knoevenagel condensation reaction<sup>37,38</sup>. However, HPW has low specific surface area and usually cannot be recovered for its solubility in many polar solvents, causing the difficulty separation and recycling, which limits its in utilization.<sup>39,40</sup> Therefore, it is imperative to develop recyclable POMs based catalysts for practical application. Various strategies for immobilization of HPW on supports have been developed including embedding HPW into metal-organic framework,41,42 adsorption on actived carbon,<sup>43,44</sup> electrostatic attachment to quanternary ammonium functionalized chloromethylated polystyrene (DMA16/CMPS),<sup>45</sup> amine-grafted graphene oxide,<sup>46</sup> exfoliated montmorillonite47 and carbon nitride materials,48,49 covalently grafted POM on mesoporous hybrid silicas<sup>50</sup> and SBA-15<sup>51</sup>. The most developed and widely used technique is electrostatic attachment of HPW to positively charged supports.<sup>52</sup> More recently, Song prepared a series of POM intercalated-layered double hydroxides (POM-LDHs) catalysts by facile ion exchange method, which showed excellent activity (99%) and selectivity (≥ 99%) in oxidation-Knoevenagel condensation reactions.<sup>53</sup> This is the first case for the efficient utilization of POM-LDH as bi-functional heterogeneous catalysts for the promotion of tandem rea-

Page 2 of 28

View Article Online DOI: 10.1039/C6CY01669C

#### Journal Name ARTICLE

ctions.

Graphitic carbon nitride  $(g-C_3N_4)$  is composed of a large number of nitrogen with potential base functionality (terminal amino groups -NH<sub>2</sub> and bridging N atoms -N-). Except for large surface area and abundant mesopores, mesoporous graphitic carbon nitride (mpg-C<sub>3</sub>N<sub>4</sub>) has more nitrogen as active sites, which can be as anchors for HPW<sup>54</sup> and show good catalytic performance in Knoevenagel condensations as active sites<sup>55,56</sup>.

Herein, HPW was immobilized on protonated mpg-C<sub>3</sub>N<sub>4</sub> via electrostatic interaction and used as a single-site bifunctional heterogeneous catalyst in the oxidation-Knoevenagel condensation tandem reaction. Due to its controllable redox and acidic properties, HPW can catalyze oxidation and efficiently Knoevenagel condensation reaction. Moreover, mpg-C<sub>3</sub>N<sub>4</sub> not only acts as support but also promotes the Knoevenagel condensation effectively. HPW/mpg-C<sub>3</sub>N<sub>4</sub> as heterogeneous catalysts can be easily recovered and reused without obvious deterioration of their structural integrity and activity.

#### 2. Experimental

#### 2.1 Materials

All the reagents were analytical purity and were used as received. Poly(ethyleneglycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123) was purchased from Sigma-Aldrich. Dicyandiamide (DCDA), phosphotungstic acid hydrate (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O), ethyl acetate, ethyl cyanocaetate and diethyl malonate were obtained from Tianjin Guangfu Fine Chemical Research Institute. 30wt% H<sub>2</sub>O<sub>2</sub> and benzyl alcohol were purchased from Tianjin Bodi Chemical Co. Ltd. Malononitrile, cinnamyl alcohol, 4-methylbenzyl alcohol, 4methoxybenzyl alcohol, 4-fluorobenzyl alcohol, 3fluorobenzyl alcohol, 2-fluorobenzyl alcohol and 2pyridinemethanol were purchased from Energy Chemical Co. Ltd.

#### 2.2 Characterization

Fourier transform infrared spectroscopy (FT-IR) spectra

were obtained on a Bio-Rad FTS 6000 system using diffuse reflectance sampling accessories. Powder X-ray diffraction (XRD) patterns were obtained using X-ray diffraction (XRD, D/max-2500 with Cu Ka radiation,  $\lambda$ =1.5406 Å). Solid-state <sup>31</sup>P nuclear magnetic resonance was performed on Varian Infinityplus 300. <sup>31</sup>P nuclear magnetic resonance (<sup>31</sup>P NMR) was obtained on Avavce 400. Thermal properties of the composites were measured by thermo gravimetric analysis (TGA). The samples were heated to 800 °C at a heating rate of 10 °C · min<sup>-1</sup> under air atmosphere on a SDT Q600. The content of W was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on Opfima 7300V. The morphology of the composites was observed by scanning electronic micrograph (SEM, JEOL JSM-5600) and transmission electron microscope (TEM, JEM-100CX). Brunauer-Emmett-Teller (BET) surface area analysis was performed using the nitrogen adsorption isotherms at 77 K using a Micromeritics Model ASAP 2020 instrument. All samples were degassed at 423 K under vacuum for 6 h. The average pore diameter and pore volume were calculated based on the Barrett-Joyner-Halenda (BJH) method. Zeta potential measurements were performed using the Zetasizer Nano ZS (Malvern Instruments) based on the dynamic light-scattering analysis. X-ray photoelectron spectroscopy (XPS) measurement was performed on PHI-5000 Versaprobe spectrometer equipped with a monochromatic Al Ka X-ray source. Ammonia temperature programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD) measurements were performed on a Micromeritics AutoChem 2920 instrument. The sample (100 mg) was pretreated at 300 °C in N<sub>2</sub> flow (30 mL/min) for 2 h and then cooled down to 50 °C. Introducing NH<sub>3</sub> in the sample tube for 30 min, saturated adsorption of NH<sub>3</sub> on the sample was obtained. Then the physically adsorbed NH<sub>3</sub> was removed by flushing the sample tube with an argon flow. TPD measurements were carried out in the range 50-550 °C at a heating rate of 10 °C/min.

#### 2.3 Catalysts preparation

**2.3.1 Preparation of mpg-C<sub>3</sub>N<sub>4</sub>.** Mpg-C<sub>3</sub>N<sub>4</sub> was obtained by self-condensation of DCDA with elimination of ammonia according to the previous method.<sup>57</sup> In a typi-

cal synthesis, P123 (7.0 g) as the soft template was firstly dissolved in 60 mL of water, and then DCDA (10 g) was added into the solution and stirred vigorously for 4 h, and subsequently dried at 100 °C in air. Then the mixture was transferred into a 50 mL crucible with a cover. The crucible was heated stepwise in muffle furnace, first 0.5 h at 250 °C, then 0.5 h at 350 °C with a heating rate of 1.7 °C·min<sup>-1</sup>. Finally it was heated to 550 °C at a rate of 3.3 °C·min<sup>-1</sup> and kept for 4 h at 550 °C. The mpg-C<sub>3</sub>N<sub>4</sub> was obtained simultaneously with the remove of soft template during the calcination.

**2.3.2 Preparation of HPW/mpg-C<sub>3</sub>N<sub>4</sub>.** The HPW/mpg-C<sub>3</sub>N<sub>4</sub> catalysts were prepared by a method of incipient wetness. A typical process was as follows: 1.0 g of mpg-C<sub>3</sub>N<sub>4</sub> was added to 5.0 mL of aqueous solution containing a certain amount of HPW under vigorous stirring at 25 °C for 12 h. The mixture was then dried for 12 h in a vacuum oven (60 °C, -0.1 MPa). The obtained samples are referred to as X wt%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (where 'X wt%' represents the weight of percent of HPW in the sample).

#### 2.4 Catalytic one-pot tandem reaction

Published on 01 December 2016. Downloaded by University of Regina on 05/12/2016 12:42:55.

The one-pot synthesis of  $\alpha,\beta$ -unsaturated compounds was carried out in a 25 mL three-necked round flask equipped with a magnetic stirrer and a reflux condenser. In a typical run, 3 mmol of benzyl alcohol, 150 mg of catalyst, 9 mmol of 30% H<sub>2</sub>O<sub>2</sub> and 3 mL of deionized water were added into the flask. The mixture was vigorously stirred at 90 °C for 3 h. Subsequently, malononitrile (6 mmol) was added into the mixture rapidly, and then the reaction mixture was further stirred for 4 h at the same temperature. The reaction mixture was extracted with ethyl acetate and the catalyst was separated by centrifugation after reaction. The organic phase was analyzed by a SP-3420A gas chromatograph (Beijing Beifen-Ruili analytical instrument Co. Ltd) equipped with a KB-Wax column (30 m, 0.32 mm id, 0.25 µm film thickness) with toluene as internal standard and products were confirmed by a Thermo Trace DSQ gas chromatograph-mass spectrometer. The recovered catalysts were washed with ethanol and deionized water

and then dried for 12 h in a vacuum oven (60  $^{\circ}$ C, -0.1 MPa). The catalysts were reused for the above tandem reaction.

## 3. Results and discussion

#### 3.1 Catalyst characterization

3.1.1 Compositional and structural information of **HPW/mpg-C<sub>3</sub>N<sub>4</sub>.** The FT-IR spectra of mpg-C<sub>3</sub>N<sub>4</sub>, HPW and HPW/mpg-C<sub>3</sub>N<sub>4</sub> are shown in Fig. 1. The characteristic band of the mpg-C<sub>3</sub>N<sub>4</sub> shows a framework band at 806 cm<sup>-1</sup>, which corresponds to the characteristic mode of the triazine units.<sup>54,58</sup> The band at 1637 cm<sup>-1</sup> is associated with C=N stretching vibration mode, and the bands at 1245, 1319 and 1403 cm<sup>-1</sup> are ascribed to aromatic C-N stretching.54,59,60 The band at 3414 cm<sup>-1</sup> may be related to NH stretching mode in the aromatic ring.<sup>61</sup> The spectrum of the HPW with Keggin structure at 1079 cm<sup>-1</sup> is assigned to the asymmetric vibrations of the P-O of tetrahedral PO<sub>4</sub>, and the bands at 984, 890 and 805 cm<sup>-1</sup> are attributed to the stretching modes of the terminal W=O, edge sharing of W-O<sub>b</sub>-W and corner sharing of W-Oc-W units, respectively.<sup>40,62-65</sup> These characteristic bands of Keggin structure are obviously observed in the FT-IR spectrum of HPW/mpg-C<sub>3</sub>N<sub>4</sub>. Furthermore, the characteristic bands of HPW in the FT-IR spectrum of HPW/mpg-C<sub>3</sub>N<sub>4</sub> have a slightly red-shift (1079 to 1075 cm<sup>-1</sup>, 890 to 884 cm<sup>-1</sup>) compared with those of HPW, indicating a strong interaction between  $[PW_{12}O_{40}]^{3}$  and mpg-C<sub>3</sub>N<sub>4</sub>.<sup>49,63</sup> The results of FT-IR suggest that HPW could be immobilized on mpg-C<sub>3</sub>N<sub>4</sub>.

Fig. 2 shows the XRD patterns of mpg-C<sub>3</sub>N<sub>4</sub>, bulk g-C<sub>3</sub>N<sub>4</sub>, HPW and HPW/mpg-C<sub>3</sub>N<sub>4</sub> with different HPW loading (20-40%). For mpg-C<sub>3</sub>N<sub>4</sub>, the strong peak located at 27.3° (d = 0.326 nm) is attributed to the interlayer stacking (002) peak of aromatic segments of the carbon nitride sheets.<sup>54,66</sup> An low-angle reflection at 13.2° (d = 0.670 nm) is connected to the (100) plane,<sup>67</sup> which is smaller in-planar distance than one tri-s-triazine unit (0.713 nm), presumably originated from the in-planar tris-triazine units with a small tilt angularity to the main layers.<sup>68</sup> However compared with those of g-C<sub>3</sub>N<sub>4</sub>, the (002) and (100) peaks of the XRD pattern of mpg-C<sub>3</sub>N<sub>4</sub>

DOI: 10.1039/C6CY01669C

#### Journal Name ARTICLE

broadened with low intensity, suggesting the effect of the geometric confinement in the nanosized pore walls.<sup>69</sup> The diffraction peaks at  $2\theta$  (in degree) = 8-11°, 18-22°, 24-30° and 33-40° are characteristic of HPW with Keggin structure.<sup>70</sup> In the XRD patterns of HPW/mpg-C<sub>3</sub>N<sub>4</sub>, the intensity of mpg-C<sub>3</sub>N<sub>4</sub> characteristic peak at 27.5° gradually weakens and the intensity of the HPW-related peak at 26.4° gradually increases with increase loading of HPW (20%-40%). The typical peaks of HPW in the XRD patterns of HPW/mpg-C<sub>3</sub>N<sub>4</sub> and its structure was well preserved.

Fig. 3A shows the solid-state <sup>31</sup>P MAS NMR spectra of HPW and 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>. The spectrum of HPW shows one signal at -15.7 ppm, which is attributed to the tetrahedral coordination of PO<sub>4</sub> in the Keggin unit.<sup>71</sup> For the solid-state <sup>31</sup>P NMR spectrum of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>, a similar signal at -15.5 ppm can be observed, indicating that the HPW have been successfully immobilized into the mpg-C<sub>3</sub>N<sub>4</sub> and the primary structure of HPW is well preserved. The results are consistent with the results of FT-IR and XRD.

In order to investigate the interaction between HPW and mpg-C<sub>3</sub>N<sub>4</sub>, HPW was substituted by HCl with the same molar of H<sup>+</sup> to obtain protonated mpg-C<sub>3</sub>N<sub>4</sub> (mpg-C<sub>3</sub>N<sub>4</sub>-H<sup>+</sup>) during the preparation of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>. As shown in Fig. 3B and Fig. S1, the zeta potential of mpg-C<sub>3</sub>N<sub>4</sub> is -22.0 mV under neutral conditions whereas the protonated mpg-C<sub>3</sub>N<sub>4</sub> is -14.8 mV, suggesting partial protonation of N (C=N, C-N and C-N(H) of mpg-C<sub>3</sub>N<sub>4</sub>)<sup>72,73</sup>. More negative charges on the surfaces of HPW/mpg-C<sub>3</sub>N<sub>4</sub> were observed with increase of HPW loading from 20% to 40%. This result demonstrated that HPW was successfully immobilized by electrostatic interaction with mpg-C<sub>3</sub>N<sub>4</sub>-H<sup>+</sup>.

XPS were performed to investigate the composition and chemical states of the elements in the 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (Fig. 4). The XPS wide scan spectrum shows that 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> is composed of P, W, O, C and N. The P 2p spectrum exhibits a broad signal peak at about 133.8 eV, indicating the existence of  $P^{5+}$  in the oxidation state.<sup>66</sup> The W 4f spectrum is deconvoluted into two peaks at 35.1 eV (4f<sub>5/2</sub>) and 37.3 eV (4f<sub>7/2</sub>) respectively, which are typically ascribed to W in the W-O bond configuration and  $W^{6+}$  in HPW.<sup>53,74</sup>

The C 1s spectrum can be deconvoluted into three peaks at 284.4, 285.2 and 288.2 eV, corresponding to the pure graphitic sites in the CN matrix (C-C), sp<sup>2</sup>-bonded to N inside the s-triazine units (N=C-N) and sp<sup>2</sup> C atoms bonded to aliphatic amine in the aromatic rings (N=C(-N)-N), respectively.<sup>75,76</sup> Additionally, the N 1s spectrum displays four deconvoluted peaks with binding energies of 398.3, 399.9, 401.3 and 403.8 eV, indicating four types of N with different bonding states on the surface of mpg- $C_3N_4$ . Among them, the three peaks of 398.3, 399.9 and 401.3 eV are ascribed to the sp<sup>2</sup>-bonded aromatic N in the triazine units (C-N=C), the bridging N bonding to carbon atoms (N-(C)<sub>3</sub> or C-N(-H)-C) and the terminal amino groups (C-NH<sub>2</sub>) due to incomplete condensation, respectively.<sup>73,76,77</sup> The peak at 403.8 eV is attributed to the positive charge effect in the heterocycles due to a small amount of protonated N of mpg-C<sub>3</sub>N<sub>4</sub>, which is consistent with the results of zeta potentials.<sup>72,73,76</sup> The results of XPS indicate the structural integrity of HPW after the immobilization onto mpg-C<sub>3</sub>N<sub>4</sub> by electrostatic interaction, which are in good agreement with the results obtained from FT-IR, XRD and solid-state <sup>31</sup>P NMR spectra.

Fig. 5 shows the TGA curves of HPW, HPW/mpg-C<sub>3</sub>N<sub>4</sub> (20%-40%) and mpg-C<sub>3</sub>N<sub>4</sub>. The TGA curve of HPW shows three weight loss steps. The first weight loss (8.3%) between 25 °C and 100 °C is due to the weight loss of physically absorbed water. The second weight loss (3.3%) between 100 °C and 250 °C is due to the weight loss of structural water. The third weight loss (0.7%) up to 600 °C results from the loss of acidic protons and the decomposition of the Keggin structure.<sup>78,79</sup> For mpg- $C_3N_4$ , a weight loss of 7.4% up to 200 °C is due to the removal of adsorbed water, and the weight loss of 92.4% between 500 °C and 730 °C is due to the direct thermal decomposition of mpg-C<sub>3</sub>N<sub>4</sub>.<sup>80</sup> The TGA curves also show that HPW/mpg-C<sub>3</sub>N<sub>4</sub> (20%, 30% and 40%) have excellent chemical stability from 25 to 500 °C. According to the above results, the actual HPW loading in HPW/mpg-C<sub>3</sub>N<sub>4</sub> are about 19.5%, 28.0% and 38.6% respectively, which are similar to the corresponding theoretical value of 20%, 30% and 40%. Additionally, the HPW loading of the catalysts was also determined by

analysis of P by ICP-AES. The HPW loading are about 18.8%, 27.6% and 38.1% respectively, which are similar to those of TGA.

 $NH_3$ -TPD was performed to investigate the acid amounts of HPW, 20%HPW/mpg-C<sub>3</sub>N<sub>4</sub> and 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (Fig. S2). The detailed explanation is shown in ESI.

3.1.2 Morphology and textural property of HPW/mpg-C<sub>3</sub>N<sub>4</sub>. The  $N_2$ adsorption-desorption isotherms and the corresponding pore size distribution (PSD curves) of curves  $g-C_3N_4$ mpg- $C_3N_4$ , 20%HPW/mpg-C<sub>3</sub>N<sub>4</sub> and 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> are shown in Fig. 6. The N<sub>2</sub> adsorption-desorption of mpg-C<sub>3</sub>N<sub>4</sub> shows a type IV isotherm pattern with a H3 hysteresis loop and two capillary condensation steps at a low relative pressure and a high relative pressure region respectively, which is characteristics of highly ordered mesoporous materials with bimodal pores.<sup>81</sup> The corresponding PSD curve of mpg-C<sub>3</sub>N<sub>4</sub> (Fig. 6 inset) also shows that the sample has two distributions with small mesopores and large mesopores. The small mesopores (the pore distribution centered at 3.89 nm) originate from the decomposition of P123 template,<sup>61</sup> while the large mesopores with a broad distribution (10.0-40.0 nm) may be assigned to either the aggregates (loose assemblages) of plate-like particles of the carbon nitride<sup>61</sup> or the coalescence of the mesopores due to the decomposition of the lower molecular weight CN polymers during the carbonization process<sup>82</sup>. For bulk g-C<sub>3</sub>N<sub>4</sub>, there is also a small hysteresis loop starting at  $p/p_0 = 0.8$ , indicating poor porosity of bulk g-C<sub>3</sub>N<sub>4</sub> compared with mpg-C<sub>3</sub>N<sub>4</sub>. The detailed textural parameters are summarized in Table 1. Mpg-C<sub>3</sub>N<sub>4</sub> has higher surface area (146  $m^2 \cdot g^{-1}$ ) and larger pore volume (0.206 cm<sup>3</sup> · g<sup>-1</sup>) than bulk g-C<sub>3</sub>N<sub>4</sub>  $(12.2 \text{ m}^2 \cdot \text{g}^{-1} \text{ and } 0.0627 \text{ cm}^3 \cdot \text{g}^{-1})$ . This result confirms that the introduction of the template favorably generation of mesospores. Compared with that of mpg-C<sub>3</sub>N<sub>4</sub> and 20%HPW/mpg-C<sub>3</sub>N<sub>4</sub>, the N<sub>2</sub> adsorption-desorption isotherm and PSD curve of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> have no significant changes, however, a slight decrease in BET surface area ( $S_{BET}$ ) and pore volume (Table 1) is observed, which is due to partial blockage of the pores by HPW on mpg-C<sub>3</sub>N<sub>4</sub>.<sup>54</sup> After the impregnation, the average pore size of mpg-C<sub>3</sub>N<sub>4</sub> decreases from 9.98 nm to 9.67 nm for

30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (9.71 nm for 20%HPW/mpg-C<sub>3</sub>N<sub>4</sub>), which indicates the mesoporous structure of mpg-C<sub>3</sub>N<sub>4</sub> can be preserved even after immobilization of HPW. Thus, due to its larger surface area and porosity, HPW/mpg-C<sub>3</sub>N<sub>4</sub> is expected to show good catalytic performance in the tandem reaction.

Fig. 7 shows the morphology of mpg-C<sub>3</sub>N<sub>4</sub> and 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>. The SEM image of mpg-C<sub>3</sub>N<sub>4</sub> exhibits the tortile flake-like texture of mpg-C<sub>3</sub>N<sub>4</sub>. Fig. 7B shows SEM image of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>, in which the mpg-C<sub>3</sub>N<sub>4</sub> sheets are shaggy with lots of wrinkles, which may be due to that the changes of the morphology of mpg-C<sub>3</sub>N<sub>4</sub> by protonation. Furthermore, there is no HPW aggregation on the mpg-C<sub>3</sub>N<sub>4</sub> surface. Fig. 7C and D show typical TEM images of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>, in which the nanosheet morphology and porous texture are clearly observed. However HPW cannot be observed obviously in the TEM images of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>, possibly due to HPW in the form of  $[PW_{12}O_{40}]^{3-}$  anion immobilized onto mpg-C<sub>3</sub>N<sub>4</sub> and well dispersed on mpg-C<sub>3</sub>N<sub>4</sub>. The similar results was also obtained by Zhu<sup>54</sup>.

#### 3.2 Catalytic Activity

HPW/mpg-C<sub>3</sub>N<sub>4</sub> was used as the catalyst for one-pot synthesis of benzylidene malononitrile (Scheme 1). The tandem reaction involves two separate steps: 1) oxidation of benzyl alcohol  $(A_1)$  to benzaldehyde  $(B_1)$  with  $H_2O_2$ and 2) Knoevenagel condensation between benzaldehyde and malononitrile to produce benzylidene malononitrile (C1). The oxidations of A1 catalyzed by 30%HPW/mpg- $C_3N_4$  with different molar ratio of  $H_2O_2/A_1$  were investigated (Fig. S3). With the increase of the molar ratio of  $H_2O_2/A_1$  from 2.0 to 3.0, the conversion of  $A_1$ increased sharply from 48.7% to 98.4%. While the molar ratio of  $H_2O_2/A_1$  further increased to 3.5, the conversion of  $A_1$  almost unchanged, but the selectivity to  $B_1$ decreased obviously. Increase of the amount of H<sub>2</sub>O<sub>2</sub> enhanced conversion of  $A_1$  to  $B_1$ . However the excess of oxidant lead to the deep oxidation with more benzoic acid formed. Considering the conversion and selectivity of the oxidation reaction, the optimized molar ratio of  $H_2O_2/A_1$ was 3.0.

#### Journal Name ARTICLE

The first oxidation step could be very important for the oxidation-Knoevenagel condensation tandem reaction. HPW, mpg-C<sub>3</sub>N<sub>4</sub>, 30%HPW/g-C<sub>3</sub>N<sub>4</sub> and 30%HPW/mpg- $C_3N_4$  were used as catalysts in oxidation (Fig. 8A). No **B**<sub>1</sub> was formed in the presence of mpg-C<sub>3</sub>N<sub>4</sub>. The HPWcontaining catalysts (HPW, 30%HPW/g-C<sub>3</sub>N<sub>4</sub> and 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>) presented high catalytic activities for  $A_1$  oxidation. High conversion of  $A_1$  (98.7%) and low selectivity to  $B_1$  (74.8%) were obtained over HPW. Moreover, HPW completely dissolved in reaction medium, leading to difficulty of catalyst recovery and recycling. 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> afforded a selectivity of 95.8% to  $\mathbf{B}_1$  with  $\mathbf{A}_1$  conversion of 98.4%. Compared with 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>, 30%HPW/g-C<sub>3</sub>N<sub>4</sub> afforded a low selectivity to  $B_1$  and low conversion of  $A_1$ . As observed from the N<sub>2</sub> adsorption-desorption isotherms and PSD carves, the large surface area and porosity for mpg-C<sub>3</sub>N<sub>4</sub> can make it more favorable for the dispersion of HPW than bulk  $g-C_3N_4$ , which is beneficial to the excellent catalytic activity.

Generally, Knoevenagel condensation reactions are promoted not only by base catalysts but also by acid catalysts. Due to its redox and acidic properties, HPW as a single-site bifunctional catalyst was able to efficiently catalyze the A1 oxidation (Fig. 8A) and Knoevenagel condensation reaction respectively (Fig. 8B). Furthermore, mpg-C<sub>3</sub>N<sub>4</sub> shows excellent catalyst activity with 97.5% conversion of  $B_1$  and 98.9% selectivity to  $C_1$  for the Knoevenagel condensation reaction compared with g- $C_3N_4$ , which is in agreement with the obtained results by Su.<sup>56</sup> Moreover, 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> exhibits a better  $B_1$ conversion (98.6%) and selectivity to  $C_1$  (99.4%) than that of 30%HPW/g-C<sub>3</sub>N<sub>4</sub>. The better Knoevenagel condensation activity of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> was due to the mesoporous structure and abundant nitrogen of mpg- $C_3N_4$ , which facilitated good dispersion of HPW and with more basic sites for the condensation reaction. Therefore, the above results suggest that the HPW/mpg- $C_3N_4$  could be used as the desired catalyst to combine both oxidation and Knoevenagel condensation reaction in a one-pot reactor.

The effects of reaction conditions such as reaction time, temperature and catalyst amount were investigated (Fig. S4). The optimized reaction conditions are reaction

time 3+1 h (oxidation for 3 h and Knoevenagel condensation for 1 h), temperature at 90 °C and catalyst amount of 150 mg. Then under the optimized conditions, the one-pot synthesis of  $C_1$  over HPW/mpg- $C_3N_4$ catalysts in water was investigated (Fig. 9). As expected, HPW was able to catalyze the oxidation-Knoevenagel tandem reaction with 96.7% conversion of A1. However, the selectivity to  $C_1$  was poor with high selectivity to benzoic acid (23.7%), which was the over oxidation product of A<sub>1</sub>. 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> and 40%HPW/mpg- $C_3N_4$  catalysts showed high  $A_1$  conversion (98.4% and compared 98.8% respectively) with of that 20%HPW/mpg-C<sub>3</sub>N<sub>4</sub> catalyst (80.0%). However, the selectivity to C1 decreased over 40%HPW/mpg-C3N4 compared with that of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>, which was due to the deep oxidation of  $B_1$  to benzoic acid over excess acidic active sites. The similar results were also obtained with A1 oxidation over VO@g-C3N4 catalyst,83 and epoxidation of cyclohexene over QAPPESK-PMo<sup>84</sup>. 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> showed the best catalytic activity in the tandem reaction with 98.4% A1 conversion and 96.2% selectivity to C1. The activity of the 30%HPW/g-C3N4 is lower than that of the 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>, which is consistent with the results of separate  $A_1$  oxidation and Knoevenagel condensation reaction. This is due to good dispersion of HPW and the cooperative effects of HPW and mpg-C<sub>3</sub>N<sub>4</sub> for the Knoevenagel condensation. A physical mixture of HPW and mpg-C<sub>3</sub>N<sub>4</sub> also promoted the tandem reaction, but it was not as efficient as the 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> catalyst likely due to increased diffusion limitations. The high efficient catalytic performance of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> in the tandem reaction benefits from the good catalytic performance of HPW in the oxidation and Knoevenagel condensation respectively. Moreover, protonated mpg-C<sub>3</sub>N<sub>4</sub> facilitates good dispersion of HPW as support, which also attributes to high catalytic performance.

A possible mechanism for oxidation-Knoevenagel tandem reaction of  $A_1$  and malononitrile over 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> is proposed (Fig. S5). The detailed explanation is also included in ESI.

To describe directly the reaction process, the one-pot tandem synthesis of  $C_1$  from  $A_1$  was carried out at different reaction time. As shown in Fig. 10A, the  $A_1$  con-

#### Journal Name ARTICLE

Published on 01 December 2016. Downloaded by University of Regina on 05/12/2016 12:42:55.

version and  $\mathbf{B}_1$  yield gradually increased to the maximum values within 3 h. After adding malononitrile into the reaction solution, the intermediate  $B_1$  yield decreased rapidly, whereas the  $C_1$  yield increased sharply within 0.5 h. The results indicate that the one-pot synthesis occurred in a consecutive manner, and the oxidation was the ratecontrolling step. The similar results were also obtained with Pd/LS-AT-OH<sup>-</sup> for the aerobic oxidation-Knoevenagel condensation reaction<sup>18</sup>. Then the kinetic study for A1 conversion over 30%HPW/mpg-C3N4 has been shown in Fig. 10B. The A<sub>1</sub> conversion and  $\ln(C_t/C_0)$ are plotted against reaction time, in which C<sub>0</sub> and C<sub>t</sub> are initial  $A_1$  concentration and the concentration at time t, respectively. The linear fit of the data indicates that the catalytic reaction follows pseudo-first-order kinetics for  $A_1$  conversion (R<sup>2</sup>=0.9947). According to the Equations (1) and (2), the rate constant k of  $A_1$  conversion can be determined to be 1.0448 h<sup>-1</sup>. The similar results were also obtained with oxidation-Knoevenagel condensation of benzyl alcohol and ethyl cyanoacetate catalyzed by polyoxometalate intercalated-layered double hydroxides (POM-LDHs)<sup>53</sup>.

$-dC_t/dt = kC_t$	(1)
$\ln(C_t/C_0) = -kt$	(2)

In order to test the general applicability and efficiency of the 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>, physical mixture of HPW and mpg-C<sub>3</sub>N<sub>4</sub>, HPW and mpg-C<sub>3</sub>N<sub>4</sub> in the tandem reactions with different substrates, various benzyl alcohol derivatives (A) and active methylene compounds were investigated (Table 2). For 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>, benzyl alcohol and cinnamyl alcohol are efficiently converted to the corresponding target products (C) with malononitrile under the same reaction conditions (Table 2, entries 1 and 2). Introducing electron donor groups at the para-position of the benzyl alcohol has no effect on the high activities with appropriate prolonged reaction time (Table 2, entries 3 and 4). However, when the electron withdrawing group substituted at the *para*-position, the decrease in conversion of A is observed (Table 2, entry 5), which indicates that the electron withdrawing group impedes the oxidation process.<sup>24,53</sup> Furthermore, 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> has different catalytic performance for aromatic alcohols with a fluorine group substituted at ortho-, meta- and para-position respectively (Table 2, entries 5-7), which can be attributed to the electron withdrawing effect and increased steric hindrance. Moreover, the heterocyclic alcohol (2-pyridinemethanol) could also be converted to corresponding products under the optimal conditions (Table 2, entry 8). When the condensation reactant malononitrile is substituted by ethyl cyanocaetate or diethyl malonate, the yield for C decreases moderately (Table 2, entries 9 and 10), which is due to the fact that malononitrile is the most active methylene compound than other used condensation substrates.<sup>18</sup> No C was formed in the presence of mpg-C<sub>3</sub>N<sub>4</sub> due to no active sites for A oxidation. For various benzyl alcohol derivatives, 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> shows good catalyst activity compared with that of HPW and physical mixture of HPW and mpg-C<sub>3</sub>N<sub>4</sub>. Thus 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> exhibits the general applicability and high efficiency for the

oxidation-Knoevenagel tandem reaction.

Table 3 summarizes the catalytic performance of various catalysts previously reported in one-pot tandem synthesis of  $C_1$  from  $A_1$ . 30%HPW/mpg- $C_3N_4$  exhibits good catalytic activity with  $H_2O_2$  as oxidant under mild reaction condition compared with other previously reported catalysts (Table 3, entries 1-8). And 30%HPW/mpg- $C_3N_4$  shows comparative catalytic activity compared with Tris-LDH- $Zn_4(PW_9)_2$  for the oxidation-Knoevenagel condensation reaction (Table 3, entries 9 and 10). Due to the properties of easy preparation, noble metal-free, stability and regeneration, 30%HPW/mpg- $C_3N_4$  is a good and efficient catalyst for oxidation-Knoevenagel tandem reaction.

### 3.3 Catalyst recycling

An important issue associated with the performance of a heterogeneous catalyst is its recovery and reusability. The HPW/mpg- $C_3N_4$  catalyst could be easily separated by centrifugation after reaction. To investigate the recyclability of the 30%HPW/mpg- $C_3N_4$  catalyst, the catalyst was recycled eight times. As summarized in Fig. 11A, the catalyst exhibits no obvious decline of the conversion of benzyl alcohol and the selectivity to benzylidene malononitrile during the eighth run. In order to confirm that the active species are not the HPW leaking from 30%HPW/mpg- $C_3N_4$  catalyst in the tandem

#### Journal Name ARTICLE

reaction, hot filtration experiment was carried out. After 1 h reaction time, the catalyst was filtered, and reaction solution was kept on stirring under the same experimental conditions. The conversion of benzyl alcohol almost remained unchanged during the investigated reaction (from 1 h to 4 h) after the hot filtration experiment (Fig. 11B). Additionally, no P was detected in the filtrate according to the <sup>31</sup>P NMR data, indicating that the catalytic activity originated from 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> other than from the dissolved HPW from the leak of catalyst. The FT-IR spectra (Fig. 1e) and XRD pattern (Fig. 2g) of the recovered 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> catalyst showed no significant differences compared with the fresh catalyst, indicating the good reusability of the catalyst in the tandem reaction. Combined with the results of catalytic performance of the reused catalyst, leaking test, FT-IR and XRD, the 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> catalyst is recoverable and recyclable.

#### 4. Conclusions

A single-site bifunctional HPW/mpg-C<sub>3</sub>N<sub>4</sub> with different HPW loading was prepared by a facile impregnation method via electrostatic interaction between HPW and protonated mpg-C3N4. According to the results of NH<sub>3</sub>-TPD, the total acid amounts of 20%HPW/mpg-C<sub>3</sub>N<sub>4</sub> and 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> are 0.385 and 0.467 mmol·g<sup>-1</sup>, respectively. 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> has good catalytic performance in the oxidation-Knoevenagel condensation tandem reaction for various substituted benzyl alcohol. The high catalytic performance of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (98.4% benzyl alcohol conversion and 96.2% selectivity to benzylidene malononitrile) is attributed to good catalytic performance of HPW in the oxidation and Knoevenagel condensation, respectively. Simultaneously, the excellent catalytic performance is also attributed to good dispersion of HPW over mpg-C<sub>3</sub>N<sub>4</sub> and the cooperative effects of HPW and mpg-C<sub>3</sub>N<sub>4</sub> for the Knoevenagel condensation. The present approach provides a promising and universal strategy for the construction of hybrid catalysts based on HPW and mesoporous materials for tandem reaction.

## Acknowledgements

This work was financially supported by the National Natural Sciences Foundation of China (Nos.2090618 and 21236001), the Natural Sciences Foundation of Hebei province (No. B2010000027, B2015202262), Tianjin Municipal Natural Science Foundation (15JCYBJC21000) and Foundation of Education Bureau of Hebei Province (QN2016152). We thank to Prof. J. Zhao for helpful comments.

## References

- 1 E. Gianotti, U. Diaz, A. Veltya and A. Corma, *Catal. Sci. Technol.*, 2013, **3**, 2677-2688.
- 2 U. P. N. Tran, K. K. A. Le and N. T. S. Phan, *ACS Catal.*, 2011, **1**, 120-127.
- 3 J. Xu, Y. Wang, J. K. Shang, Q. Jiang and Y. X. Li, *Catal. Sci. Technol.*, 2016, **6**, 4192-4200.
- 4 J. Xu, K. Shen, B. Xue and Y. X. Li, *J. Mol. Catal. A: Chem.*, 2013, **372**, 105-113.
- 5 V. N. Panchenko, M. M. Matrosova, J. Jeon, J. W. Jun, M. N. Timofeeva and S. H. Jhung, *J. Catal.*, 2014, **316**, 251-259.
- 6 F. Pang, M. Y. He and J. P. Ge, *Chem. Eur. J.*, 2015, **21**, 1-10.
- 7 Y. Q. Jia, Y. J. Fang, Y. K. Zhang, H. N. Miras and Y. F. Song, *Chem. Eur. J.*, 2015, **21**, 14862-14870.
- 8 G. B. B. Varadwaj, S. Rana and K. M. Parida, *Dalton Trans.*, 2013, **42**, 5122-5129.
- 9 K. M. Parida, S. Mallick, P. C. Sahoo and S. K. Rana, *Appl. Catal. A: Gen.*, 2010, **381**, 226-232.
- 10 G. Postole, B. Chowdhury, B. Karmakar, K. Pinki, J. Banerji and A. Auroux, J. Catal., 2010, 269, 110-121.
- 11 A. Dhakshinamoorthy and H. Garcia, *ChemSusChem.*, 2014, 7, 2392-2410.
- 12 L. L. Chng, N. Erathodiyil and J. Y. Ying, Acc. Chem. Res., 2013, 46, 1825-1837.
- 13 J. M. Lee, Y. Na, H. Han and S. Chang, *Chem. Soc. Rev.*, 2004, **33**, 302-312.
- 14 J. C. Wasilke, S. J. Obrey, R. T. Baker and G. C. Bazan, *Chem. Rev.*, 2005, **105**, 1001-1020.

- 15 N. R. Shiju, A. H. Alberts, S. Khalid, D. R. Brown and G. Rothenberg, *Angew. Chem.*, 2011, **123**, 9789-9793.
- 16 L. Zhong, C. Anand, K. S. Lakhi, G. Lawrence and A. Vinu, *Sci. Rep.*, 2015, 5, 12901.1-12901.8.
- 17 L. C. Lee, J. Lu, M. Weck and C. W. Jones, ACS Catal., 2016, 6, 784-787.
- 18 L. Xu, C. G. Li, K. Zhang and P. Wu, ACS Catal., 2014, 4, 2959-2968.
- 19 R. Goyal, B. Sarkar, N. Lucus and A. Bordoloi, *ChemCatChem*, 2014, 6, 3091-3095.
- 20 F. Zhang, H. Y. Jiang, X. Y. Li, X. T. Wu and H. X. Li, *ACS Catal.*, 2014, **4**, 394-401.
- 21 T. Toyao, M. Saito, Y. Horiuchi and M. Matsuoka, *Catal. Sci. Technol.*, 2014, **4**, 625-628.
- 22 D. K. Wang and Z. H. Li, *Catal. Sci. Technol.*, 2015, 5, 1623-1628.
- 23 D. Jagadeesan, Appl. Catal. A: Gen., 2016, 511, 59-77.
- 24 Y. Qi, Y. Luan, X. Peng, M. Yang, J. Y. Hou and G. Wang, *Eur. J. Inorg. Chem.*, 2015, 2015, 5099-5105.
- 25 C. Chen, H. M. Yang, J. Z. Chen, R. Zhang, L. Guo, H. M. Gan, B. N. Song, W. W. Zhu, L. Hua and Z. S. Hou, *Catal. Commun.*, 2014, **47**, 49-53.
- 26 W. J. Ang, Y. S. Chng and Y. L. Lam, *RSC Adv.*, 2015, 5, 81415-81428.
- 27 B. Sarmah, R. Srivastava, P. Manjunathan and G. V. Shanbhag, ACS Sustainable Chem. Eng., 2015, 3, 2933-2943.
- 28 Y. Horiuchi, D. D. Van, Y. Yonezawa, M. Saito, S. Dohshi, T. H. Kim and M. Matsuoka, *RSC Adv.*, 2015, 5, 72653-72658.
- 29 C. S. Hinde, W. R. Webb, B. K. J. Chew, H. R. Tan, W. H. Zhang, T. S. A. Horbd and R. Raja, *Chem. Commun.*, 2016, **52**, 6557-6560.
- 30 M. R. Farsani, E. Assady, F. Jalilian, B. Yadollahi and H. A. Rudbari, *J. Iran. Chem. Soc.*, 2015, **12**, 1207-1212.
- 31 W. Zhao, Y. S. Zhang, B. C. Ma, Y. Ding and W. Y. Qiu, *Catal. Commun.*, 2010, **11**, 527-531.
- 32 Y. Ding, W. Zhao, H. Hua and B. C. Ma, *Green Chem.*, 2008, **10**, 910-913.
- 33 C. Ragupathi, J. J. Vijaya, S. Narayanan, S. K. Jesudoss and L. J. Kennedy, *Ceram. Int.*, 2015, **41**, 2069-2080.
- 34 B. Karimi, F. B. Rostami, M. Khorasani, D. Elhamifar

and H. Vali, Tetrahedron, 2014, 70, 6114-6119.

- 35 Y. Leng, J. Wang, D. Zhu, M. Zhang, P. Zhao, Z. Long and J. Huang, *Green Chem.*, 2011, **13**, 1636-1639.
- 36 Y. Leng, P. P. Zhao, M. J. Zhang and J. Wang, J. Mol. Catal. A: Chem., 2012, 358, 67-72.
- 37 H. A. Oskooie, M. M. Heravi, F. Derikvand and M. Khorasani, Synthetic Commun., 2006, 36, 2819-2823.
- 38 B. Viswanadham, P. Jhansi, K. V. R. Chary, H. B. Friedrich and S. Singh, *Catal Lett*, 2016, **146**, 364-372.
- 39 Y. J. Chen, R. Tan, W. G. Zheng, Y. Y. Zhang, G. W. Zhao and D. H. Yin, *Catal. Sci. Technol.*, 2014, 4, 4084-4092.
- 40 B. L. Li, J. Li, X. M. Wang, Z. X. Wan and L. C. Wang, *Kinet. Catal.*, 2013, **54**, 69-75.
- 41 X. L. Yang, L. M. Qiao and W. L. Dai, *Micropor. Mesopor. Mat.*, 2015, 211, 73-81.
- 42 F. M. Zhang, Y. Jin, J. Shi, Y. J. Zhong, W. D. Zhu and M. S. El-Shall, *Chem. Eng. J.*, 2015, **269**, 236-244.
- 43 L. Y. Liu, Y. Zhang and W. Tan, *Ultrason. Sonochem.*, 2014, **21**, 970-974.
- 44 L. Y. Liu, Y. Zhang and W. Tan, *Front. Chem. Sci. Eng.*, 2013, 7, 422-427.
- 45 H. F. Wang, L. P. Fang, Y. F. Yang, R. B. Hu and Y. J. Wang, *Appl. Catal. A: Gen.*, 2016, **520**, 35-43.
- 46 W. F. Zhang, Q. S. Zhao, T. Liu, Y. Gao, Y. Li, G. L. Zhang, F. B. Zhang and X. B. Fan, *Ind. Eng. Chem. Res.*, 2014, **53**, 1437-1441.
- 47 H. F. Wang, L. Zhang, Y. F. Yang, L. P. Fang and Y. J. Wang, *Catal. Commun.*, 2016, **87**, 27-31.
- 48 J. J. He, H. Q. Sun, S. Indrawirawan, X. G. Duan, M. O. Tade and S. B. Wang, *J. Colloid Interf. Sci.*, 2015, 456, 15-21.
- 49 K. X. Li, L. S. Yan, Z. X. Zeng, S. L. Luo, X. B. Luo, X. M. Liu, H. Q. Guo and Y. H. Guo, *Appl. Catal. B: Environ.*, 2014, **156-157**, 141-152.
- 50 X. J. Luo and C. Yang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 7892-7902.
- 51 E. Grinenval, J. M. Basset and F. Lefebvre, J. Inorg. Chem., 2013, 2013, 1-8.
- 52 C. L. Hill, O. A. Kholdeeva, in: M. G. Clerici, in Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications, ed. O. A. Kholdeeva, John Wiley & Sons, Inc. Hoboken,

DOI: 10.1039/C6CY01669C

Journal Name ARTICLE

2013, cha. 6, pp. 263-319.

- 53 K. Liu, Y. Q. Xu, Z. X. Yao, H. N. Miras and Y. F. Song, *ChemCatChem*, 2016, **92**, 112-117.
- 54 Y. F. Zhu, M. Y. Zhu, L. H. Kang, F. Yu and B. Dai, *Ind. Eng. Chem. Res.*, 2015, **54**, 2040-2047.
- 55 M. B. Ansari, H. Jin, M. N. Parvin and S. E. Park, *Catal. Today*, 2012, **185**, 211-216.
- 56 F. Z. Su, M. Antoniettia and X. C. Wang, *Catal. Sci. Technol.*, 2012, **2**, 1005-1009.
- 57 Y. Wang, X. C. Wang, M. Antonietti and Y. J. Zhang, *ChemSusChem*, 2010, **3**, 435-439.
- 58 J. Xu, F. Wu, Q. Jiang and Y. X. Li, *Catal. Sci. Technol.*, 2014, **5**, 447-454.
- 59 J. A. Singh, S. H. Overbury, N. J. Dudney, M. J. Li and G. M. Veith, ACS Catal., 2012, 2, 1138-1146.
- 60 S. Kumar, T. Surendar, B. Kumar, A. Baruah and V. Shanker, *J. Phys. Chem. C*, 2013, **117**, 26135-26143.
- 61 W. Z. Shen, L. W. Ren, H. Zhou, S. C. Zhang and W. B. Fan, *J. Mater. Chem.*, 2011, 21, 3890-3894.
- 62 J. Liu, Y. Liu, W. Yang, H. Guo, F. Fang and Z. H. Tang, J. Mol. Catal. A: Chem., 2014, 393, 1-7.
- 63 G. Q. Luo, L. H. Kang, M. Y. Zhu and B. Dai, *Fuel Process. Technol.*, 2014, **118**, 20-27.
- 64 B. S. Li, Z. X. Liu, C. Y. Han, W. Ma and S. J. Zhao, *J. Colloid Interface Sci.*, 2012, **377**, 334-341.
- 65 L. Chen and B. Bai, *Int. J. Photoenergy*, 2013, **2013**, 6687-6692.
- 66 Z. S. Li, S. Y. Yang, J. M. Zhou, D. H. Li, X. F. Zhou, C. Y. Ge and Y. P. Fang, *Chem. Eng. J.*, 2014, 241, 344-351.
- 67 D. A. Giannakoudakis, M. Seredych, E. R. Castellón and T. J. Bandosz, *ChemNanoMat*, 2016, **79**, 187-209.
- 68 S. X. Min and G. X. Lu, J. Phys. Chem. C, 2012, 116, 19644-19652.
- 69 F. Goettmann, A. Fischer, M. Antonietti and A. Thomas, *Angew. Chem. Int. Ed.*, 2006, **45**, 4467-4471.
- 70 H. F. Wang, R. B. Hu, Y. F. Yang, M. D. Gao and Y. J.

Wang, Catal. Commun., 2015, 70, 6-11.

- 71 R. Liu, X. N. Xia, X. Z. Niu, G. Z. Zhang, Y. B. Lu, R. F. Jiang and S. L. He, *Appl. Clay Sci.*, 2015, **105-106**, 71-77.
- 72 T. Y. Ma, Y. H. Tang, S. Dai and S. Z. Qiao, *Small*, 2014, **10**, 2382-2389.
- 73 W. J. Ong, L. L. Tan, S. P. Chai, S. T. Yong and A. R. Mohamed, *Nano Energy*, 2015, **13**, 757-770.
- 74 E. V. Ramos-Fernandez, C. Pieters, B. V. D. Linden, J. Juan-Alcañiz, P. Serra-Crespo, M. W. G. M. Verhoeven, H. Niemantsverdriet, J. Gascon and F. Kapteijn, J. Catal., 2012, 289, 42-52.
- 75 J. Xu, F. Wu, H. T. Wu, B. Xue, Y. X. Li and Y. Cao, *Micropor. Mesopor. Mat.*, 2014, **198**, 223-229.
- 76 W. J. Ong, L. K. Putri, L. L. Tan, S. P. Chai and S. T. Yong, *Appl. Catal. B: Environ.*, 2016, **180**, 530-543.
- 77 Q. Su, J. Sun, J. Q. Wang, Z. F. Yang, W. G. Cheng and S. J. Zhang, *Catal. Sci. Technol.*, 2014, 4, 1556-1562.
- 78 L. Zhang, H. Q. He, R. K. A. Rasheed, W. J. Zhou, Y. H. Xue, O. L. Ding and S. H. Chan, *J. Power Sources*, 2013, **221**, 318-327.
- 79 R. Liu, X. Z. Niu, X. N. Xia, Z. B. Zeng, G. Z. Zhang and Y. B. Lu, *RSC Adv.*, 2015, 5, 62394-62401.
- 80 J. J. Zhu, P. Xiao, H. L. Li and S. A. C. Carabineiro, ACS Appl. Mater. Inter., 2014, 6, 16449-16465.
- 81 Z. K. Zhao, Y. T. Dai, J. H. Lin and G. R. Wang, *Chem. Mater.*, 2014, 26, 3151-3161.
- 82 S. N. Talapaneni, S. Anandan, G. P. Mane, C. Anand, D. S. Dhawale, S. Varghese, A. Mano, T. Moricd and A. Vinu, *J. Mater. Chem.*, 2012, **22**, 9831-9840.
- 83 S. Verma, R. B. N. Baig, M. N. Nadagouda and R. S. Varma, *ACS Sustainable Chem. Eng.*, 2016, **4**, 1094-1098.
- 84 Z. H. Weng, J. Y. Wang, S. H. Zhang, C. Yan and X. G. Jian, *Appl. Catal. A: Gen.*, 2008, **339**, 145-150.



Fig. 1 FT-IR spectra (A) and partial enlarged detail (B) of mpg- $C_3N_4$  (a), 20%HPW/mpg- $C_3N_4$  (b), 30%HPW/mpg- $C_3N_4$  (c), 40%HPW/mpg- $C_3N_4$  (d), R-30%HPW/mpg- $C_3N_4$  (e) and HPW (f).



Fig. 2 XRD patterns of bulk g- $C_3N_4$  (a), mpg- $C_3N_4$  (b), HPW (c), 20%HPW/mpg- $C_3N_4$  (d), 30%HPW/mpg- $C_3N_4$  (e), 40%HPW/mpg- $C_3N_4$  (f) and R-30%HPW/mpg- $C_3N_4$  (g).



Fig. 3 Solid-state <sup>31</sup>P NMR spectra (A) and zeta potential (B).



Published on 01 December 2016. Downloaded by University of Regina on 05/12/2016 12:42:55. Intensity (a.u.)

Fig. 4 XPS wide scan spectra of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (A) and P 2p, W 4f, C 1s and N 1s XPS spectrum of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (B–E).



Fig. 5 TGA analysis of HPW (a), 40%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (b), 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (c), 20%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (d) and mpg-C<sub>3</sub>N<sub>4</sub> (e).



Fig. 6  $N_2$  adsorption-desorption isotherms of mpg-C<sub>3</sub>N<sub>4</sub> (a), 20%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (b), 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (c) and g-C<sub>3</sub>N<sub>4</sub> (d) and the corresponding PSD curves (inset).



Fig. 7 SEM images of mpg-C<sub>3</sub>N<sub>4</sub> (A) and 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (B) and TEM of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (C, D).



**Fig. 8** Benzyl alcohol oxidation (A) and Knoevenagel condensation reaction (B) using different catalysts, conversion of  $A_1$  (black), selectivity to  $B_1$  (red), selectivity to benzoic acid (green), conversion of  $B_1$  (blue) and selectivity to  $C_1$  (pink). Reaction conditions: (A)  $A_1$  (3 mmol),  $H_2O_2/A_1 = 3 : 1$  (molar ratio),  $H_2O$  (3 mL), 90 °C, 3 h; (B)  $B_1$  (3 mmol),  $B_1$ /malononitrile = 1 : 2 (molar ratio),  $H_2O$  (3 mL), 90 °C, 4 h for g- $C_3N_4$  and mpg- $C_3N_4$ , 1 h for others.



**Fig. 9** One-pot oxidation-Knoevenagel tandem reaction, conversion of  $A_1$  (black), selectivity to  $C_1$  (pink), selectivity to  $B_1$  (red) and selectivity to benzoic acid (green). Reaction conditions:  $A_1$  (3 mmol),  $H_2O$  (3 mL), 90 °C, 3 + 1 h,  $H_2O_2/A_1$ /malononitrile = 3 : 1 : 2 (molar ratio), catalyst: a) catalyst 150 mg, b) HPW 40 mg, c) physical mixture of HPW 40 mg and mpg- $C_3N_4$  110 mg.



**Fig. 10** (A) Reaction profile of oxidation-Knoevenagel condensation of  $A_1$  and malononitrile, (a)  $A_1$ , (b)  $B_1$  and (c)  $C_1$ . (B) Kinetic study for conversion of  $A_1$  over 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>. Reaction conditions:  $A_1$  (3 mmol),  $H_2O$  (3 mL), 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (150 mg),  $H_2O_2/A_1$ /malononitrile = 3 : 1 : 2 (molar ratio), 90 °C, 3 + 1 h.



**Fig. 11** (A) Recyclability test of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> catalyst; (B) Hot filtration experiments: (a) with the presence of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>; (b) 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> was hot filtrated at 1 h.

-				
	sample	Pore volume $(cm^3 \cdot g^{-1})$	$S_{BET} (m^2 \cdot g^{-1})$	Average pore size <sup>a</sup> (nm)
	g-C <sub>3</sub> N <sub>4</sub>	0.0627	12.2	21.3
	mpg-C <sub>3</sub> N <sub>4</sub>	0.206	146	9.98
	20%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	0.0814	124	9.71
	30%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	0.0562	107	9.67

Table 1 Textural parameters of g-C <sub>3</sub> N <sub>4</sub> , mp	g-C <sub>3</sub> N <sub>4</sub> , 20%HPW	$V/mpg-C_3N_4$ and 30%	%HPW/mpg-C <sub>3</sub> N <sub>4</sub>

a) Average pore size determined by the desorption branch of isotherms.

		HPV	V/mpg	J-C <sub>3</sub> N <sub>4</sub>	$R_2 R_2$	$R_2$		
		H <sub>2</sub> O	2	H <sub>2</sub> O	× <sub>1</sub> Ο	$R_1 R_3$		
	A				В	С		
Entry	А	$R_2$	R <sub>3</sub>	Time (h)	Catalyst	Conversion A (%)	Selecti	vity (%)
							С	В
					30%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	98.4	96.2	0.421
1	U OH	CN	CN	3+1	HPW+mpg-C <sub>3</sub> N <sub>4</sub>	86.2	82.8	0.346
					HPW	96.7	74.8	1.53
	ОН				30%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	97.6	98.4	2.39
2		CN	CN	3+1	HPW+mpg-C <sub>3</sub> N <sub>4</sub>	88.5	85.2	2.21
	~				HPW	97.1	77.3	3.67
	ОН				30%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	98.9	96.8	0.343
3	H <sub>3</sub> C	CN	CN	3+1	HPW+mpg-C <sub>3</sub> N <sub>4</sub>	87.3	81.6	0.374
					HPW	98.4	75.2	1.83
	ОН				30%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	95.3	96.2	1.42
4	н <sub>3</sub> со	CN	CN	5+1	HPW+mpg-C <sub>3</sub> N <sub>4</sub>	85.3	83.7	0.415
					HPW	96.2	74.3	2.32
	ОН				30%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	84.4	95.6	0.563
5	F	CN	CN	5+1	HPW+mpg-C <sub>3</sub> N <sub>4</sub>	76.8	82.1	0.392
					HPW	86.0	70.9	2.84
	ОН				30%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	61.9	96.9	0.421
6		CN	CN	5+1	HPW+mpg-C <sub>3</sub> N <sub>4</sub>	57.6	84.3	0.418
	F				HPW	63.4	71.9	3.04
					30%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	53.7	97.1	0.371
7	F	CN	CN	5+1	HPW+mpg-C <sub>3</sub> N <sub>4</sub>	51.9	87.1	0.336
					HPW	60.4	70.8	3.27
	$\langle$				30%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	87.6	95.3	0.430
8	С	CN	CN	7+1	HPW+mpg-C <sub>3</sub> N <sub>4</sub>	85.2	87.7	0.371
					HPW	89.8	74.3	1.89

Table 2 Oxidation-Knoevenagel tandem reactions with different substrates

Published on 01 December 2016. Downloaded by University of Regina on 05/12/2016 12:42:55.

Entry	А	R <sub>2</sub>	R <sub>3</sub>	Time (h)	Catalyst	Conversion A (%)	Selectiv	vity (%)
							С	В
					30%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	98.6	91.6	5.36
9	ОН	CN	COOEt	3+4	HPW+mpg-C <sub>3</sub> N <sub>4</sub>	86.8	79.8	4.36
					HPW	96.9	67.1	8.24
	~ ~				30%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	98.4	82.7	13.1
10	ОН	COOEt	COOEt	3+4	HPW+mpg-C <sub>3</sub> N <sub>4</sub>	86.5	71.6	12.3
					HPW	96.6	57.9	15.8

Table 2 (continued) Oxidation-Knoevenagel tandem reactions with different substrates

Reaction conditions: A (3 mmol), H<sub>2</sub>O (3 mL), 90 °C, H<sub>2</sub>O<sub>2</sub>/A/active methylene compound = 3 : 1 : 2 (molar ratio), catalyst: (a) 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> 150 mg, (b) physical mixture of HPW 40 mg and mpg-C<sub>3</sub>N<sub>4</sub> 110 mg and (c) HPW 40 mg.

	1 5	2		10 5 4	1	5	
Entry	Catalyst	Oxidant	Temperature	Time	Conversion	Selectivity to C <sub>1</sub>	Ref
Endy	Culuiyst	Omulant	(°C)	(h)	(%)	(%)	iter.
$1^{a}$	Zr-MOF-NH <sub>2</sub>	$O_2$	90	48	100	91	21
2 <sup>a</sup>	NH <sub>2</sub> -MIL-101(Fe)	$O_2$	25	40	88	72	22
3	Au@MIL-53(NH <sub>2</sub> )	$O_2$	100	13	99	99	24
4	Pd/LS-AT-OH <sup>-</sup>	$O_2$	85	11	89.6	88.3	18
5	Pd <sub>1</sub> -Au <sub>1</sub> /LDH	$O_2$	80	2.5	99	98.0	25
6	Bispidine-copper	$O_2$	40	7	-	79 (86)	26
7	OMS-2-SF	$O_2$	85/70	9.5	99.5	84.5	27
8	OMS-2-U	$O_2$	85/70	9.5	91.6	88.9	27
9	Tris-LDH-Zn4(PW9)2	$\mathrm{H}_{2}\mathrm{O}_{2}$	80	4	99	99	53
10	30%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	$\mathrm{H}_{2}\mathrm{O}_{2}$	90	4	98.4	96.2	This study

rubie e companison of catalytic activity between 507011 (7)mpg C314 and reported catalys
--

a Photocatalytic aerobic oxidation-Knoevenagel condensation reaction by light irradiation.



Scheme 1 Oxidation-Knoevenagel tandem reaction over HPW/mpg-C<sub>3</sub>N<sub>4</sub>.

# Table of contents entry

A single-site bifunctional catalyst for oxidation-Knoevenagel condensation tandem reaction was prepared by immobilizing  $H_3PW_{12}O_{40}$  on mpg- $C_3N_4$  via electrostatic interaction.

