

## Electronic Supplementary Information

### **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**

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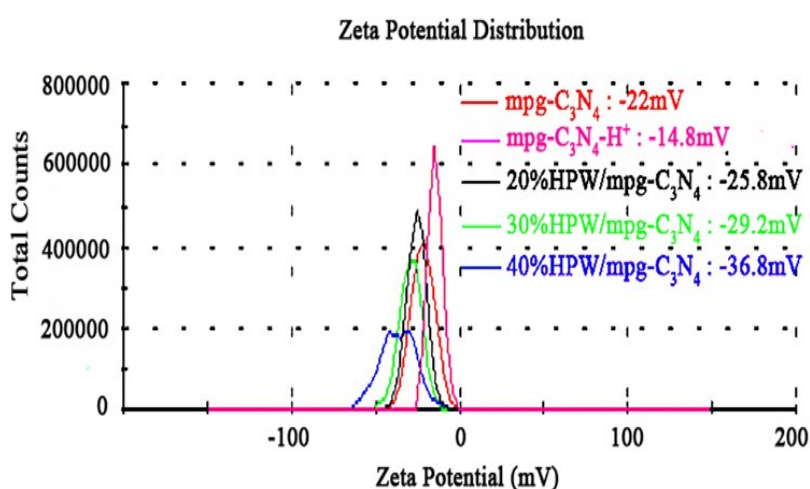
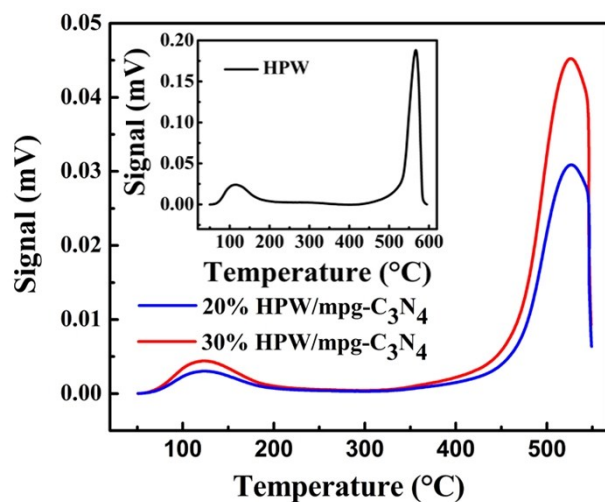


Fig. S1 Zeta potential distribution.

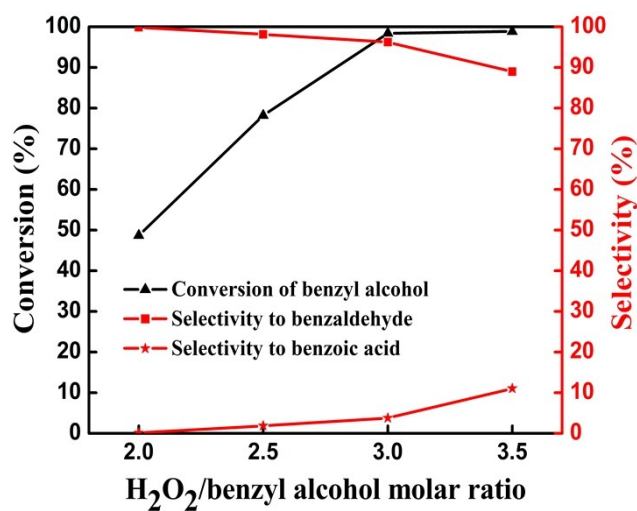
NH<sub>3</sub>-TPD was performed to investigate the acid amounts of HPW, 20%HPW/mpg-C<sub>3</sub>N<sub>4</sub> and 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>. As shown in Fig. S2, the NH<sub>3</sub>-TPD spectra show two desorption peaks, which are the low temperature desorption peak around 120 °C and the high temperature desorption peak around 525 °C, respectively. It indicates that the existence of weak and strong acidic sites on HPW, 20%HPW/mpg-C<sub>3</sub>N<sub>4</sub> and 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>.<sup>1,2</sup> The quantitative results are summarized in Table S1. The total acid amount of HPW determined by NH<sub>3</sub>-TPD is 2.11 mmol·g<sup>-1</sup>. Compared with that of 20%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (0.385 mmol·g<sup>-1</sup>), the acid amount of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> (0.467 mmol·g<sup>-1</sup>) increases with the increase of HPW loading. The similar results were also obtained in HPW supported on acid-activated palygorskite.<sup>3</sup>



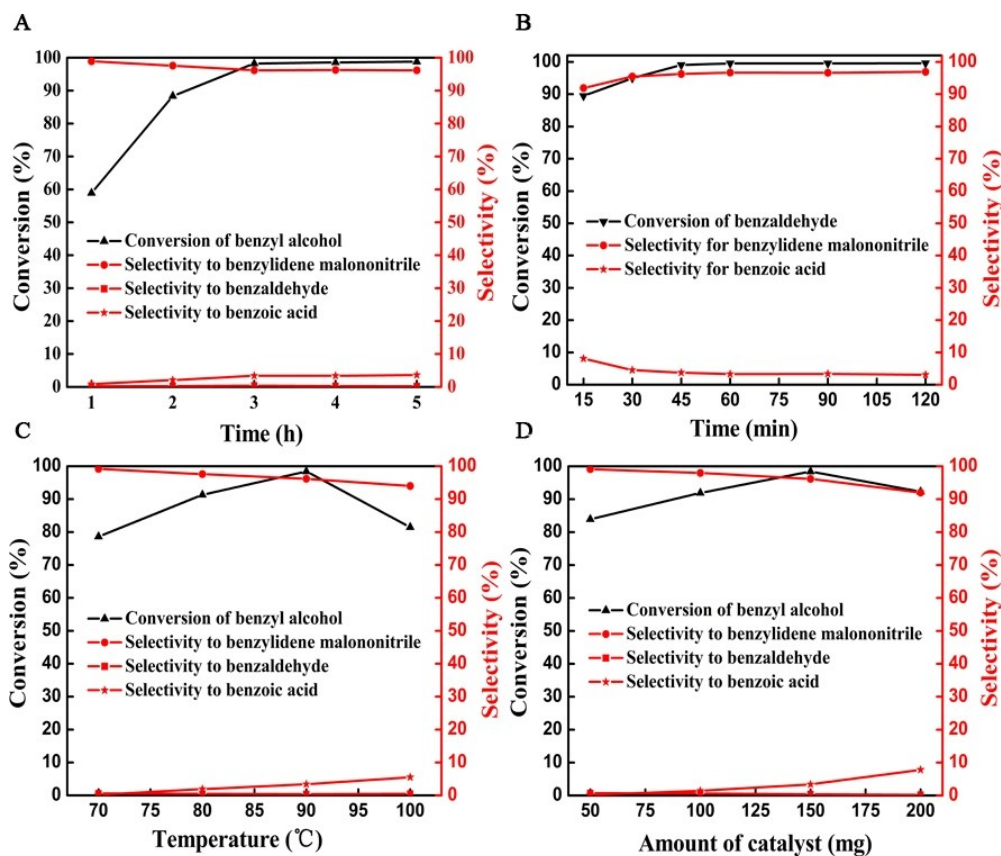
**Fig. S2** NH<sub>3</sub>-TPD spectra of HPW, 20%HPW/mpg-C<sub>3</sub>N<sub>4</sub> and 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>.

**Table S1** 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> determined by NH<sub>3</sub>-TPD

Sample	Acid amount (mmol·g <sup>-1</sup> )		
	Weak acid sites	Strong acid sites	Total acidity
HPW	0.402	1.71	2.11
20%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	0.168	0.217	0.385
30%HPW/mpg-C <sub>3</sub> N <sub>4</sub>	0.194	0.273	0.467



**Fig. S3** The effects of H<sub>2</sub>O<sub>2</sub> amount on the oxidation of benzyl alcohol over 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>.



**Fig. S4** The effects of oxidation time (A), Knoevenagel condensation time (B), reaction temperature (C) and catalyst amount (D) on the tandem reaction over 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>.

A possible mechanism for oxidation-Knoevenagel tandem reaction of **A**<sub>1</sub> and malononitrile over 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> is proposed in Scheme 2. For the **A**<sub>1</sub> oxidation, H<sub>2</sub>O<sub>2</sub> reacts with HPW to generate active peroxo intermediate, which is responsible for the **A**<sub>1</sub> oxidation to **B**<sub>1</sub> with loss of H<sub>2</sub>O molecule.<sup>4,5</sup> Then the carbonyl group of **B**<sub>1</sub> is activated by HPW (acidic sites) on the surface of 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub> to generate a carbocation. The Lewis-base site of mpg-C<sub>3</sub>N<sub>4</sub> abstracts a proton from the methylene carbon of malononitrile to generate the nucleophilic species,<sup>6</sup> which attacks the carbonyl group of **B**<sub>1</sub> with C-C bond formation followed by dehydration to form the product **C**<sub>1</sub>.<sup>7-9</sup>

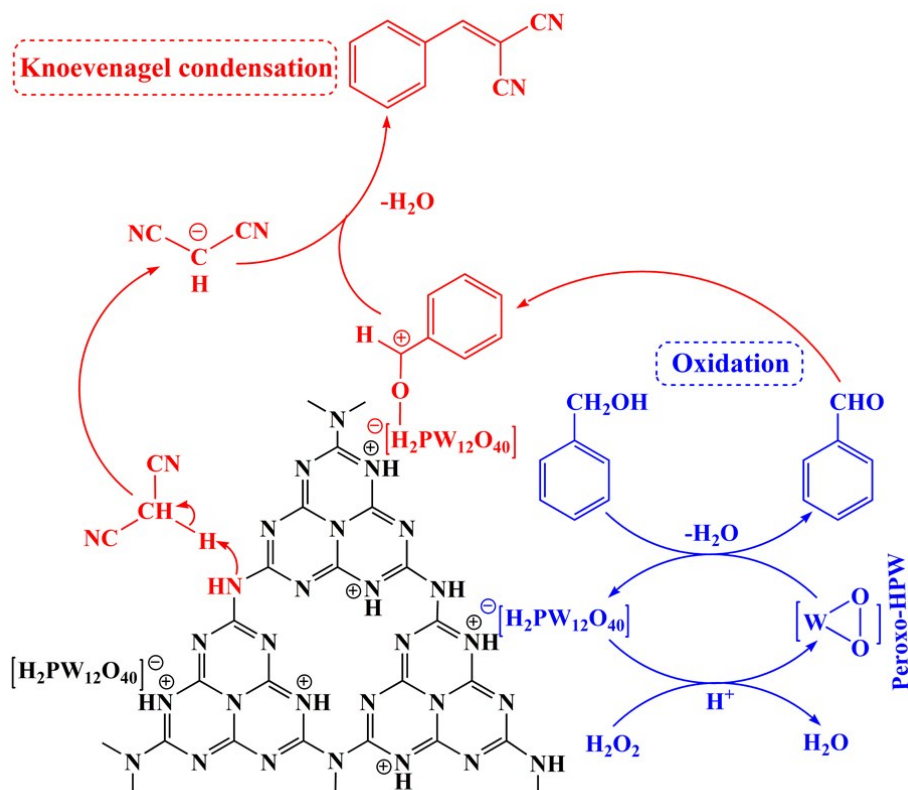


Fig. S5 Proposed mechanism for oxidation-Knoevenagel tandem reaction of **A**<sub>1</sub> and malononitrile over 30%HPW/mpg-C<sub>3</sub>N<sub>4</sub>.

## References

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