

Electronic Supplementary Information

Heteropolyacid salts of N-methyl-2-pyrrolidonium as highly efficient and reusable catalysts for Prins reactions of styrenes with formalin

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1 Reagents

N-Methyl-2-pyrrolidone (GR grade) was purchased from Alfa Aesar Chemical Company. 12-Tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$), 12-phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$), 12-silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$), and α -methylstyrene were purchased from Sinopharm Chemical Reagent Co., Ltd. 4-Methylstyrene was purchased from aladdin. Styrene was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Formalin (37 wt.% aqueous solution of formaldehyde) was purchased from Guangdong Xilong Chemical Co., Ltd. HZSM-5 (Si/Al=28) was purchased from Nankai University Catalyst Co., Ltd., and CT-252, a sulfonic acid cation-exchanged macroporous polystyrene resin, was from Purolite International Company Ltd. All chemicals were used as received without further purification.

2 Experimental

2.1 Preparation of organic heteropolyacid salts

N-Methyl-2-pyrrolidone (3 mmol) was charged into a 250 mL flask, followed by the dropwise addition of aqueous solution of 12-phosphotungstic acid (1 mmol) under stirring, then it was further stirred at ambient temperature for 12 h. Afterwards, the resulting mixture was moved into a rotary evaporator for dehydration in vacuum at 80 °C for 12 h to obtain the final product, the white solid powder of the phosphotungstic acid salt of N-Methyl-2-pyrrolidonium that is designated as $[\text{NMP}]_3\text{PW}$ (yield: 96.8%). $[\text{NMP}]\text{H}_2\text{PW}$ and $[\text{NMP}]_2\text{HPW}$ were prepared by similar procedures with their respective stoichiometric compositions. *i.e.*, 1 mmol and 2 mmol of N-Methyl-2-pyrrolidone, respectively. $[\text{NMP}]_3\text{PMo}$ and $[\text{NMP}]_4\text{SiW}$ were prepared accordingly using 12-phosphomolybdic acid and 12-silicotungstic acid as the raw materials, respectively. Triphenyl(3-sulfopropyl)phosphonium phosphotungstate ($[\text{TPSPP}]_3\text{PW}$) was synthesized according to our previously reported method (W. Zhang, Y. Leng, D. Zhu, Y. Wu, J. Wang, *Catal. Commun.*, 2009, **11**, 151).

2.2 General procedure of Prins reactions

All Prins cyclization reactions were carried out in a 25 mL round-bottomed flask equipped with a reflux condenser, a magnetic stirrer and an oil bath. In a typical reaction, 20 mmol of styrene (α -methylstyrene or 4-Methylstyrene) and 0.4 mmol (1.27 g) of the $[\text{NMP}]_3\text{PW}$ catalyst were successively added into the 37 wt.% aqueous solution of formaldehyde (formalin, containing 90 mmol of formaldehyde), then the reaction mixture was stirred at 95 °C for 3 h under reflux. During the reaction, the solid catalyst turned out to be an insoluble liquid-like phase. After reaction, it was a liquid triphasic system. The upper layer was the organic phase, the middle was aqueous phase and the bottom was the catalyst. The catalyst could be recovered simply by decantation. Afterwards, the recovered catalyst was dried to resume its solid state that was then reused for the next run. In order to measure the catalyst reusability, a six-run operation was carried out without adding any fresh catalyst. For analyzing the product, the product mixture was extracted by the *n*-heptane solution of ethyl acetate ($v(n\text{-heptane})/v(\text{ethyl acetate}) = 5/1$), and the extract was analyzed by a gas chromatography equipped with a FID detector. *n*-Dodecane was used as the internal standard.

2.3 Elemental analysis

Elemental analysis was performed on a CHN elemental analyzer (FlashEA 1112, Eager 300 Software).

2.4 XRD patterns

X-ray power diffraction (XRD) patterns were obtained on the Brüker D8 Advance diffractometer using the Ni-filtered CuK α radiation at 40 kV and 20 mA ($\lambda=0.1542$ nm).

2.5 Measurement of acid strength

The acid strength (H_0) of [NMP] $_3$ PW, [NMP] $_3$ PMo and [NMP] $_4$ SiW were measured with Hammett indicators, including dicinnamalacetone ($pK_a = -3.0$), anthraquinone ($pK_a = -8.2$) and p-nitrotoluene ($pK_a = -11.35$). They were $-8.2 < H_0 < -3.0$.

2.6 Determination of melting points

The melting point was measured on the X-4 microscopic melting-point detector (Shanghai Cany precision instrument Co., Ltd). The upper limit of the instrument is 250 °C. The melting points of [NMP] $_3$ PW, [NMP] $_3$ PMo and [NMP] $_4$ SiW were detected to be higher than 250 °C.

2.7 ^1H - NMR data

^1H - NMR spectra were recorded on a Brüker DPX 300 spectrometer (400 MHz) at ambient temperature in DMSO.

[NMP] $_3$ PW: δ_{H} 1.901 (m, 2H), 2.140 (t, 2H), 2.673 (s, 3H), 3.308 (t, 2H), 8.930 (b, 1H).

[NMP] $_3$ PMo and [NMP] $_4$ SiW gave similar ^1H NMR results to [NMP] $_3$ PW.

2.8 FT-IR data

FT-IR spectra for samples in KBr disks were recorded on Nexus 870 FT-IR spectrometer.

[NMP] $_3$ PW: IR (KBr, v/cm^{-1}) 3427, 1701, 1640, 1080, 981, 894, 807 cm^{-1} .

[NMP] $_3$ PMo: IR (KBr, v/cm^{-1}) 3442, 1701, 1637, 1063, 962, 878, 800 cm^{-1} .

[NMP] $_4$ SiW: IR (KBr, v/cm^{-1}) 3414, 1618, 1015, 975, 921, 881, 792 cm^{-1} .

3 Figures and schemes

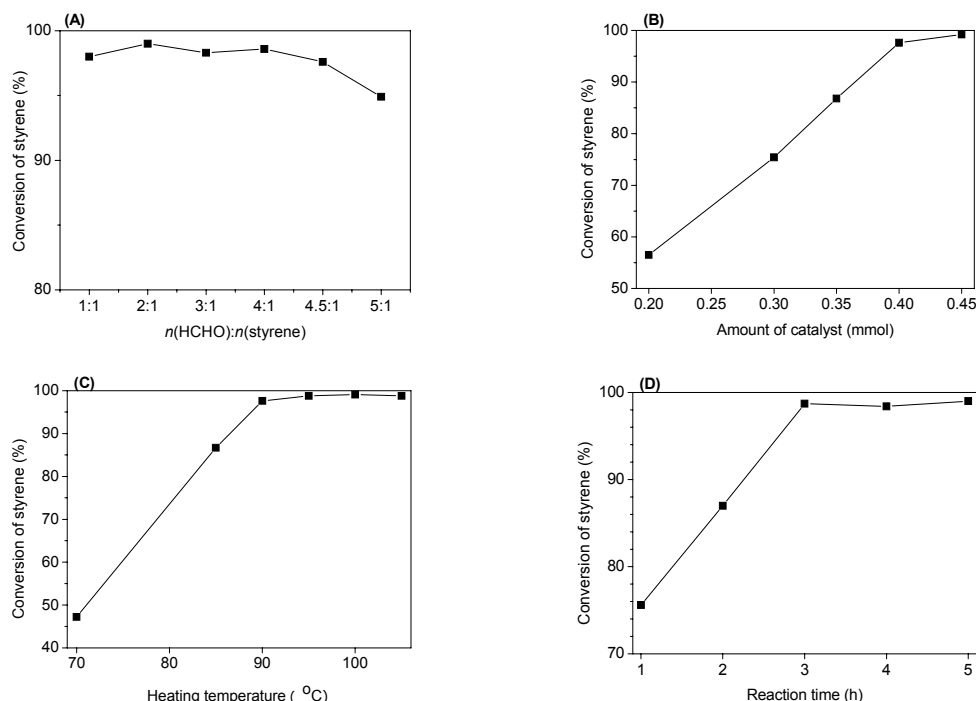


Fig. S1 Conversion of styrene in the Prins cyclization of styrene with formalin over [NMP] $_3$ PW catalyst as a function of reaction conditions.

(A) molar ratio of formaldehyde to styrene, (B) amount of catalyst, (C) heating temperature, (D) reaction time. Reaction conditions: 1.27 g (0.4 mmol) of catalyst, 20 mmol of styrene, 90 mmol of formaldehyde (37 wt.% formalin), 95 °C, 3 h; for each figure there is one specific parameter changed in X axis.

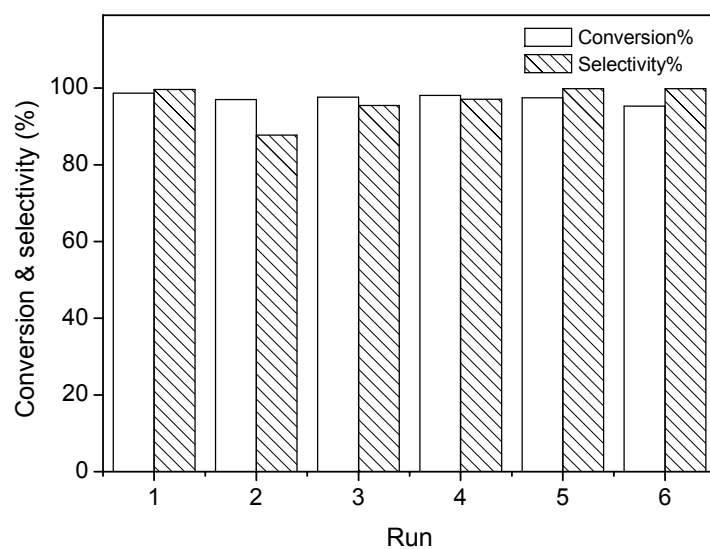


Fig. S2 The six-run test of the catalytic reusability of $[\text{NMP}]_3\text{PW}$ for Prins reaction of styrene with formalin. Reaction conditions: 1.27 g (0.4 mmol) of catalyst, 20 mmol of styrene, 90 mmol of formaldehyde (37 wt.% formalin), 95 °C, 3 h.

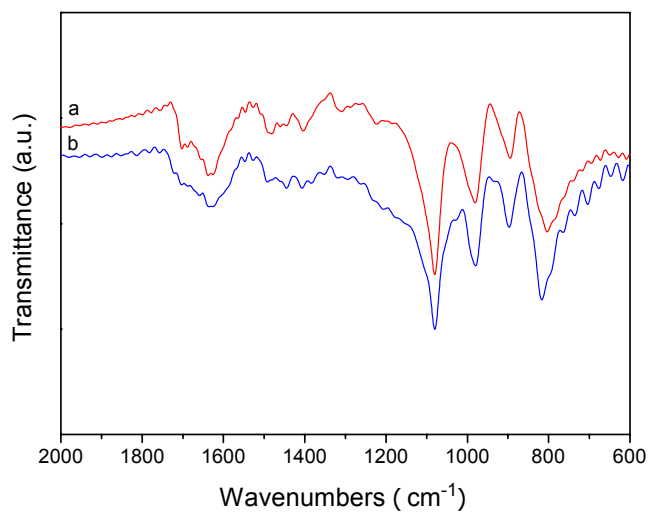
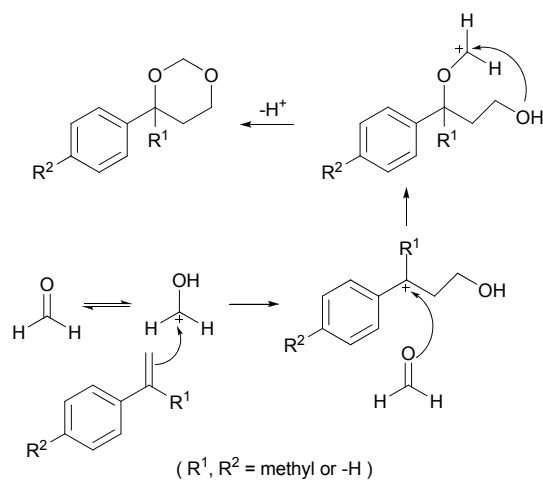


Fig. S3 FT-IR spectra of (a) fresh $[\text{NMP}]_3\text{PW}$ and (b) six-run recycled $[\text{NMP}]_3\text{PW}$.



Scheme S1 Classical mechanism of the Prins cyclization of styrene with formaldehyde.