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# COMMUNICATION

## Heteropolyacid salts of N-methyl-2-pyrrolidonium as highly efficient and reusable catalysts for Prins reactions of styrenes with formalin<sup>+</sup>

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New organic heteropolyacid (HPA) salts prepared by exchanging counter protons of Keggin HPAs with N-methyl-2-pyrrolidonium proved to be highly efficient, conveniently recoverable, and steadily reusable heterogeneous catalysts for the organic solvent-free Prins reactions of styrenes with formalin.

1,3-Dioxane derivatives, important intermediates and solvents for organic syntheses, are mainly produced from Prins reactions of olefins with aldehydes over acidic catalysts.<sup>1</sup> As a kind of polyoxometalates (POMs), heteropolyacids (HPAs) are emerging as new environmentally benign acidic catalysts for various organic transformations.<sup>2</sup> Keggin and Wells-Dawson type HPAs have been reported to be highly active homogeneous catalysts for Prins reactions of styrene with paraformaldehyde in the presence of organic solvents, however, when paraformaldehyde was replaced by an aqueous solution of formaldehyde (formalin) without additional solvents, a greener process, the conversion of styrene dropped drastically.3 In order to employ HPAs as recoverable heterogeneous catalysts, they are immobilized onto porous carriers, nevertheless, this approach always suffers from the leaching of active species and decrease in activity.<sup>4</sup> Therefore, the preparation of highly active, conveniently recoverable and steadily reusable HPA-based catalysts for organic solvent-free Prins reactions still remains as a challenging issue.

Currently, ionic liquids (ILs) are used as novel reaction media due to their negligible volatility, high thermal stability, alterable solubility, and structural versatility.5 For Prins cyclization of styrene with formaldehyde, the acidic IL 1butyl-3-methyl-imidazolium hydrogen sulfate [BMIm]HSO4 was revealed to be a very effective catalyst that could be recycled by vacuum distillation.<sup>6</sup> For the purpose of more convenient isolation of the catalyst, various efforts have been devoted to the supported ILs;<sup>7</sup> for example, 1-octyl-3-methyl-imidazolium

bis(trifluoromethane)sulfonimide salt [C8MIm]NTf2 was coated onto sulfonate silica, showing a better activity in Prins reactions towards 1,3-dioxane.7b However, the complex preparation of the catalyst and the need for the expensive IL [C8MIm]NTf2 are still less satisfactory.

It is noticeable that if the bulky and high valent heteropolyanion was used as the inorganic moiety for ILs, the obtained ionic compounds always possessed such high melting points that cannot be used as liquid media as conventional ILs.8 Nevertheless, this may be a new approach to obtain HPA-based solid hybrid catalysts with IL-like compositions. Thus, we recently developed a new family of solid acids by combining Keggin heteropolyanions with IL-forming organic cations functionalized by propane sulfonate, and found that the catalysts were highly active, conveniently recoverable, and steadily reusable in esterifications.9

It is well-known that N-methyl-2-pyrrolidone can be readily protonated to give N-methyl-2-pyrrolidonium (NMP),<sup>10</sup> which is occasionally used as the organic cation to produce acidic ILs.11 However, NMP has never been combined with a HPA anion. In this study, we prepare a group of organic HPA salts via the reaction of N-methyl-2-pyrrolidone with Keggin HPAs, and use the resulting solids as acidic catalysts for Prins cyclizations of styrene and its derivatives with formalin, as shown in Scheme 1 exemplified by [NMP]<sub>3</sub>PW (phosphotungstic acid salt of NMP). The new catalyst presented very high conversion and selectivity



Scheme 1 Synthesis of the [NMP]<sub>3</sub>PW catalyst and the [NMP]<sub>3</sub>PWcatalyzed Prins cyclization of styrene and its derivatives with an aqueous solution of formaldehyde.

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and allowed convenient recovery and steady reuse, leading to an organic solvent-free heterogeneous green Prins reaction.

Fig. 1(A) compares the FT-IR spectrum of [NMP]<sub>3</sub>PW with those of N-methyl-2-pyrrolidone and  $H_3PW_{12}O_{40}$ . The four characteristic bands for the Keggin structure of neat H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> appeared at 1080, 978, 895 and 812 cm<sup>-1</sup>, assignable to  $v_{as}$ (P-O),  $v_{as}$ (W=O) (terminal oxygen),  $v_{as}$ (W-O<sub>b</sub>-W) (corner-sharing oxygen) and  $v_{as}$  (W–O<sub>c</sub>–W) (edge-sharing oxygen), respectively.<sup>4c</sup> For [NMP]<sub>3</sub>PW, the four strong Keggin-structured peaks also occurred, but with a blue shift of 978 cm<sup>-1</sup> to 981 cm<sup>-1</sup> and a red shift of 812 cm<sup>-1</sup> to 807 cm<sup>-1</sup>. Meanwhile, the band at 1669 cm<sup>-1</sup> for the stretching vibration of the C=O bond in *N*-methyl-2-pyrrolidone shifted to 1701 cm<sup>-1</sup> for [NMP]<sub>3</sub>PW. Moreover, <sup>1</sup>H NMR data of [NMP]<sub>3</sub>PW indicated the NMP structure for the organic moiety (ESI<sup>†</sup>). These features allow us to draw the conclusion that both organic and inorganic moieties of [NMP]<sub>3</sub>PW retain their original structures. The observed band shifts imply the formation of the ionic linkage between the amide cation and the heteropolyanion. Elemental analysis results (C: 5.52 wt%, N: 1.29 wt%, H: 0.92%) confirm the catalyst's chemical composition of  $(C_5H_{10}NO)_3PW_{12}O_{40}$  with theoretical concentrations of C: 5.67 wt%, N: 1.32 wt%, and H: 0.95%.



**Fig. 1** FT-IR spectra (A): (a) *N*-methyl-2-pyrrolidone, (b)  $H_3PW_{12}O_{40}$ , and (c) [NMP]<sub>3</sub>PW; and XRD patterns (B): (a)  $H_3PW_{12}O_{40}$ , and (b) [NMP]<sub>3</sub>PW.

XRD patterns of [NMP]<sub>3</sub>PW and the pure  $H_3PW_{12}O_{40}$  (both after drying at 100 °C for 2 h) are illustrated in Fig. 1(B).  $H_3PW_{12}O_{40}$  displayed a set of well resolved sharp diffraction peaks for the secondary structure of the HPA crystal. For [NMP]<sub>3</sub>PW, some of the above featured peaks (*e.g.*, at 2 $\theta$ of 10.19, 20.59, 23.19, 25.41, 29.39 and 34.6°) could still be detected. This provides a strong proof for the formation of the similar crystal structure of the organic HPA salt of NMP to that of Keggin phosphotungstic acid. However, the replacement of protons by the large organic cation NMP results in the substantial decrease in the long-range order of the crystal lattice, demonstrated by the drastically lowered peak intensities.

In addition,  $[NMP]_3PW$  was detected to possess a high melting point of above 250 °C (ESI†), mostly due to the strong electrostatic interaction between the organic cation and the high valent heteropolyanion. Also, its solid nature might associate with the extended hydrogen bonding networks between anions and cations, implied by the 3427 cm<sup>-1</sup> IR band for the H–O vibration (ESI†). In addition, it was observed to be insoluble in not only non-polar but also many polar solvents, such as water, methanol, ethanol, formaldehyde, styrene derivatives, and so on. Its acid strength (H<sub>0</sub>) was between -8.2 and -3.0 tested by

**Table 1** Reactivities of Prins reactions of styrene and its derivativeswith formalin over  $[NMP]_3PW$  and related catalysts<sup>a</sup>

Entry	Catalyst	$\mathbf{R}^{d}$	t/h	$T/^{\circ}\mathrm{C}$	C <sup>e</sup> (%)	Sf (%)
1	Without	4.5:1	3	95	11.7	0.0
2	$H_3PW_{12}O_{40}$	4:1	3	90	87.3	98.9
3	[NH <sub>4</sub> ] <sub>3</sub> PW	4.5:1	3	95	98.7	61.7
4	[NMP] <sub>3</sub> PW	4.5:1	3	95	98.7/95.3 <sup>g</sup>	99.6/99.8 <sup>g</sup>
5	[NMP] <sub>3</sub> PMo	4:1	3	90	98.8	99.1
6	[NMP] <sub>4</sub> SiW	4:1	3	90	82.8	99.0
7	CT-252	4.5:1	3	95	75.2	99.0
8	HZSM-5	4.5:1	3	95	31.5	60.6
9	$98\%H_2SO_4$	4:1	8	90	96.6	66.4
10 <sup>b</sup>	[NMP]₃PW	4.5:1	3	95	98.5	99.1
11 <sup>c</sup>	[NMP] <sub>3</sub> PW	4.5:1	2	90	98.7	89.1
12	[NMP] <sub>2</sub> HPW	4:1	3	90	97.6	76.2
13	NMPH <sub>2</sub> PW	4:1	3	90	65.4	18.1
14	[TPSPP] <sub>3</sub> PW <sup>h</sup>	4.5:1	3	95	95.8	84.2

<sup>*a*</sup> Reaction conditions: 0.4 mmol of catalyst (1.27 g for entries 7 and 8, and 0.21 g for entry 9), 20 mmol of styrene ( <sup>*b*</sup> 4-methylstyrene, and <sup>*c*</sup>  $\alpha$ -methylstyrene). <sup>*d*</sup> Molar ratio of formaldehyde to styrene. <sup>*c*</sup> Conversion of styrene (100%) = mmol converted styrene/mmol initial styrene. <sup>*f*</sup> Selectivity of 4-phenyl-1,3-dioxane (100%) = mmol 4-phenyl-1,3-dioxanes/mmol converted styrene. <sup>*s*</sup> Conversion and selectivity at the sixth run for testing the catalyst reusability. <sup>*h*</sup> Triphenyl(3-sulfopropyl)phosphonium phosphotungstate.

Hammett indicators (ESI<sup>†</sup>), which is comparable to those of Hform zeolites.<sup>12</sup> All these properties enable the newly synthesized organic HPA salt of NMP to act as the heterogeneous catalyst for lots of acid-catalyzed organic reactions.

Table 1 lists the catalytic performance of various catalysts for Prins reaction of styrene with formalin. No dioxane product was detected without using a catalyst (entry 1). The pure  $H_3PW_{12}O_{40}$ showed a high selectivity with a considerable conversion, however, it caused a homogeneous system that leads to difficulty in catalyst isolation (entry 2). The insoluble inorganic HPA salt of ammonium caused the catalysis to be heterogeneous, but gave only low selectivity of 61.7% (entry 3). Very interestingly, the new organic HPA salt [NMP]<sub>3</sub>PW not only resulted in a heterogeneous reaction, but also exhibited almost exclusive selectivity to 4-phenyl-1,3-dioxane of 99.6% coupled with a very high conversion of 98.7% (entry 4; also see Fig. S1 (ESI<sup>+</sup>) for optimization of reaction conditions). When using Keggin 12-phosphomolybdic anion (PMo<sub>12</sub>O<sub>40</sub><sup>3-</sup>) and 12-silicotungstic anion  $(SiW_{12}O_{40}^{4-})$  to replace  $PW_{12}O_{40}^{3-}$ , the prepared organic HPA salt catalysts [NMP]<sub>3</sub>PMo and [NMP]<sub>4</sub>SiW also provided good to excellent performance (entries 5 and 6), indicating the generalizability of the catalyst design strategy. Furthermore, in comparison with the usual solid acidic catalysts of HZSM-5 zeolite and sulfonated resin CT-252, and the conventionally used liquid acidic catalyst of concentrated sulfuric acid (entries 7-9), the new organic HPA salt catalysts are much more active and/or selective in this Prins reaction.

Two styrene derivatives, 4-methylstyrene and  $\alpha$ -methylstyrene, were also used as the substrates over the [NMP]<sub>3</sub>PW catalyst (entries 10 and 11). Again, the catalyst resulted in very high conversion and selectivity that are much higher than the previous efforts for the synthesis of 4-methyl-4-phenyl-1,3-dioxane from  $\alpha$ -methylstyrene using trifluoromethanesulfonic acid<sup>14</sup> and the Wells–Dawson HPA H<sub>8</sub>P<sub>2</sub>Mo<sub>16</sub>V<sub>2</sub>O<sub>62</sub><sup>3a</sup> as the catalysts.

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HPA salts of NMP are solids; however, they became an insoluble liquid-like phase under working conditions of Prins reactions. Thus, the catalysts actually brought about a liquid–liquid heterogeneous catalysis system. At the end of the reaction, the liquid-like catalyst was at the bottom of the mixture and 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. During the six-run test of the catalyst reusability without adding any fresh catalyst, no appreciable loss of conversion and selectivity was observed (entry 4; also see Fig. S2 in ESI† for details). IR spectrum for the reused catalyst showed a very similar profile to the fresh one (Fig. S3 in ESI†), suggesting a very durable structure of the catalyst.

It is known from the classical mechanism for Prins cyclization of the alkene with formaldehyde (Scheme S1 in ESI<sup>†</sup>),<sup>1c</sup> the formation of protonated formaldehyde by the chemisorption of formaldehyde on the acidic site of the catalyst is the key to the overall reaction. For [NMP]<sub>3</sub>PW of this study, the carbonyl of the amide is suggested to be able to stabilize the protonated formaldehyde by sharing its electron with the electron-deficient center of the protonated formaldehyde (Scheme 2),<sup>13</sup> through which the whole reaction could be facilitated effectively. Another interpretation of the excellent performance of [NMP]<sub>3</sub>PW may be relative to the pseudoliquid nature of HPAs, i.e., the secondary structure of HPAs allows the permeating of polar substrates into the bulk of HPAs, through which the mass transfer is accelerated, just as in the case of a homogeneous medium.<sup>2c</sup> It is thus proposed that the reactant formaldehyde could penetrate into the bulk of [NMP]<sub>3</sub>PW, and then be chemisorbed onto the acid site of NMP to generate the protonated formaldehyde that was further stabilized therein according to Scheme 2. It is thus clear that NMP plays a crucial role in accounting for the excellent catalytic performance.



Scheme 2 Stabilization effect of the amide group in [NMP]<sub>3</sub>PW on the reaction intermediate of the protonated formaldehyde.

partially NMP-substituted [NMP]<sub>2</sub>HPW The and [NMP]H<sub>2</sub>PW catalysts (entries 12 and 13) gave lower conversions with the decrease of NMP content, corresponding to the above proposal. Moreover, the very low selectivity is suggested to relate to the two different types of acid sites: one from the remaining protons and the other from the NMP moiety. In addition, the control catalyst [TPSPP]<sub>3</sub>PW (entry 14), a typical sample in our earlier findings whose acidity comes from sulfonated groups,9 presented a lower yield of 4-phenyl-1,3-dioxane in comparison with [NMP]<sub>3</sub>PW, mostly due to the absence of the stabilization effect on the protonated formaldehyde arising from NMP shown in Scheme 2.

### Conclusions

In summary, we have designed and prepared a group of new organic HPA salts by combining NMP (*N*-methyl-2-pyrrolidium) with Keggin type heteropolyanions. They are characterized as high-melting point ionic solids, and proved to be novel heterogeneous green catalysts for Prins reactions of styrene and its derivatives with an aqueous solution of formaldehyde (formalin). The new catalyst [NMP]<sub>3</sub>PW exhibited a very high yield of 98.3% and very high selectivity of 99.6% toward the target product 4-phenyl-1,3-dioxane in Prins cyclization of styrene with formalin, and gave quite stable reusability demonstrated by a six-run cycling test. The pseudoliquid behavior of the HPA salt catalyst and the stabilization effect of the carbonyl in the amide on the protonated formaldehyde of the reaction intermediate, together with its solid nature and insolubility, are proposed to account for the excellent catalytic performance.

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