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The catalytic effect of anion-exchanged supported ionic liquid on aza-Michael-type addition

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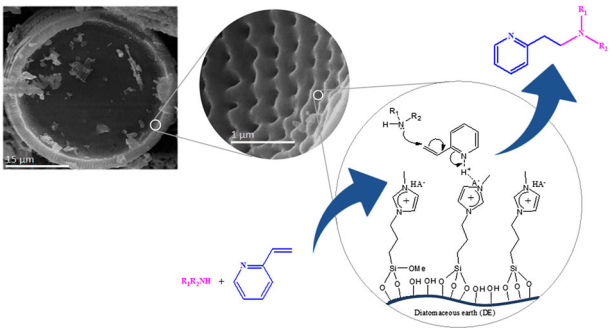
Abstract An effective synthesis of anion-exchanged supported ionic liquids using diatomaceous earth as solid support and its catalytic effect on the aza-Michael-type addition is described. Anionic polytungstophosphate and bisulfate ion are used in the anion-exchange step in catalyst design. In addition, the aza-Michael-type addition of various amines to 2- and 4-vinyl pyridine was examined in this article. The catalytic system can be separated from the reaction mixture and recycled in subsequent reactions. The structure of anion-exchanged supported ionic liquid on diatomaceous earth was studied by XRD, FT-IR, SEM, TGA and BET techniques. The structure of organic products was determined by ^{1}HNMR, ^{13}CNMR, FTIR, CHN and MASS spectroscopy.

Graphical Abstract



Keywords Anion-exchanged supported ionic liquid · Diatomaceous earth · Anionic polytungstophosphate · Aza-Michael-type addition · Catalysis

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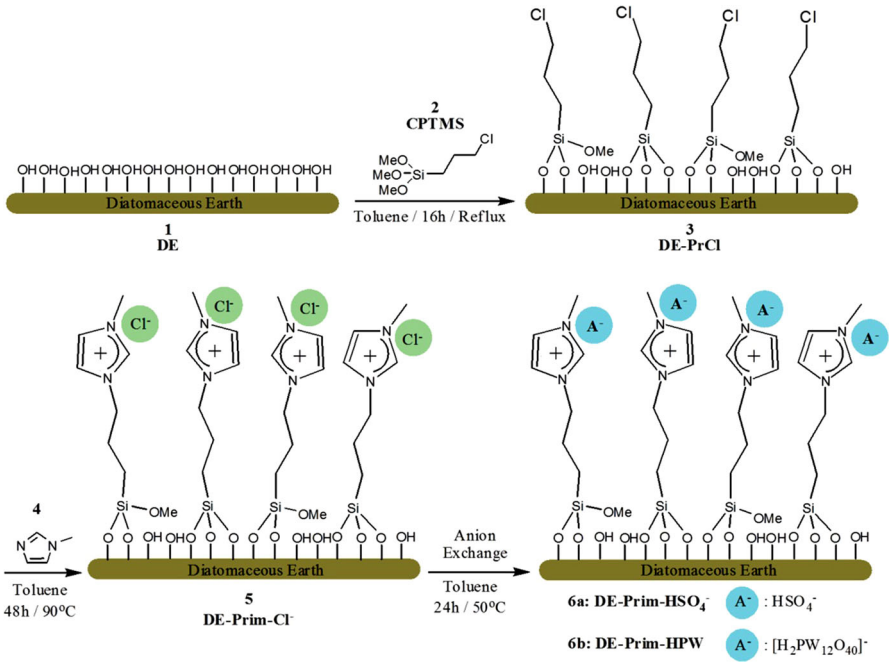
Introduction

Diatomaceous earth (DE), known as diatomite or diatoms, is the most abundant form of silica on earth naturally composed of amorphous hydrated silica (SiO_2–nH_2O) [1]. Hydrophilic properties, high porosity, strong acid resistance, low thermal conductivity, low density and excellent thermal resistance are among DE unique physical and chemical characteristics [2–5] which make it ideal for a variety of applications such as supports, porous catalysts, and adsorbents [6, 7]. Due to these special characteristics, DE was applied as a porous support in this research. Surface functionalization of DE by the introduction of covalently bonded functional groups to the outer DE surfaces is a helpful approach to increase selectivity and loading capacity of a catalytically active species [8–10].

The polyoxometalate compounds have been used as efficient catalysts in various chemical transformations due to their strong Brønsted acidity, thermal stabilities, lower corrosivity and higher catalytic activity [11–16]. However, the problems in recovery at the end of reactions limits the catalytic action of polyoxometalates [17]. In this research, (3-Mercaptopropyl)trimethoxysilane, which has a chloro group (–Cl) at the end, was used as a linker to modify the surface of DE with acidic ionic liquid. The efficiency of modified DE with two types of Brønsted and Lewis acidic ionic liquids was properly investigated. So, the immobilization of the polyoxometalates on the solid support will supply mild treatment in the production process and open up a possibility for their applications in the chemical or pharmaceutical industry.

Immobilization of ionic liquids by covalent connection on the surface of solid supports is directed to heterogenization of homogeneous catalysts. These catalytic systems that mix the properties of both homogeneous and heterogeneous catalysts have the advantage of the elevated surface area, increased activity, selectivity and sufficiently recovering the catalyst system. A number of techniques have been published for the preparation of supported ionic liquids [18–22]. Many ionic liquid catalytic systems containing polyoxometalate anions have been prepared and examined in some useful organic transformations [23–28]. Although much research has been done in the field of supported ionic liquids, the immobilization of anionic polyphosphotungstate on the diatomaceous earth covalently functionalized with (3-chloropropyl)trimethoxysilane (CPTMS) as reported in this manuscript, has a great novelty and may also create new opportunities for attractive research. The activity of heterogeneous catalysts is often comparable to their corresponding homogeneous analogs, illustrating that the heterogenization of homogeneous catalysts could be successful.

In this study, a supported IL design has been applied for the immobilization of an anionic polyphosphotungstate derivative and bisulfate anion. We want to describe an appropriate procedure for the application of anionic acids in supported IL for the synthesis of some valuable pharmaceutical molecules (Scheme 1). Phosphotungstic acid ($H_3PW_{12}O_{40}{\cdot}nH_2O$) as a polyoxometalate and sulfuric acid as a Brønsted acid were used in this research.

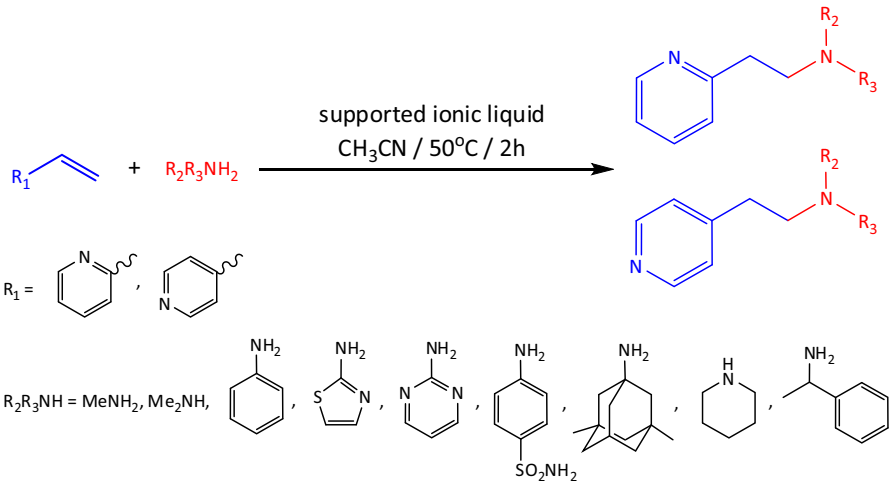


Scheme 1 Anion exchange in supported IL covalently bounded on the DE surfaces

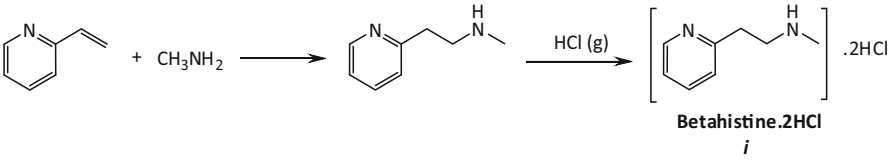
Much work has gone into the development of efficient techniques for the aza-Michael-type addition of amines to activated vinyl compounds. The aza-Michael-type addition has been catalyzed by various acids and bases in which a number of undesired reactions may have taken place, such as polymerization of vinyl compounds. Vinyl compounds, specially pre-activated vinyl compounds such as 2- and 4-vinyl pyridines used in aza-Michael-type addition in this research, have a considerable tendency to perform polymerization reactions especially in the presence of acidic catalysts, which significantly reduces the reaction overall yield. So, efficient approaches are needed for the development of mild catalytic systems for the aza-Michael-type addition. A number of alternative methodologies using catalytic systems incorporating ionic liquids have been reported [29–31]. In continuation of our previous research on the supported ionic liquids [23, 32–35], herein we report an efficient method for aza-Michael-type addition of amines to 2-vinyl pyridine and 4-vinyl pyridine catalyzed by anion-exchanged supported ionic liquids (Scheme 2).

Betahistine dihydrochloride (***i***) as an anti-vertigo drug is synthesized via the aza-Michael-type addition of methylamine to vinyl pyridine followed by addition of hydrogen chloride gas to the intermediate (Scheme 3).

The search for general, effective synthesis of the abovementioned compound under moderate conditions is of ongoing benefit for organic chemists.



Scheme 2 Aza-Michael-type addition of amines to 2-vinylpyridine and 4-vinylpyridine catalyzed by anion-exchanged supported ionic liquids



Scheme 3 The synthetic method of betahistine dihydrochloride ***i*** starting with 2-vinyl pyridine

Experimental

Materials and general techniques

Materials totally were purchased from Fluka or Merck Chemical Companies. Progression of the reactions was checked by TLC using silica gel SIL G/UV 254 plates. Melting points were recorded with an Electrothermal-9100 apparatus. NMR spectra were recorded in $CDCl_3$ on a Brucker Avance DPX instrument at 400 and 300 MHz, respectively; δ is reported in parts per million (ppm) and J in Hz. The morphology of particles was checked employing a scanning electron microscope (AIS2300C SEI scanning electron microscope) at an accelerating voltage of 25 kV. Fourier transform infrared spectra were achieved by a BRUKER EQUINOX 55 Fourier-transform spectrophotometer using the KBr pellet technique. The X-ray diffraction (XRD) patterns were reported with a Philips X'Pert MPD diffractometer equipped with Cu Kα radiation ($\lambda = 0.154$ nm) in the range 10–80° (2θ) at a speed of 0.05°/min. The specific surface areas (S_{BET}) of particles were measured by the BET method, and the pore size distributions were determined using the Barrett–Joyner–Halenda (BJH) method. Thermogravimetric analysis (TGA) was carried out using a

Perkin–Elmer thermobalance at a heating rate of 10 °C min^{-1} from 20 to 600 °C in a nitrogen gas flow to evaluate the amount of organic groups bound to the DE surface.

Preparation and characterization of catalyst

Preparation and characterization of modified DE (DE-PrCl, 3)

Diatomaceous earth was functionalized with (3-chloropropyl)trimethoxysilane (CPTMS) according to the literature with some modifications [36]. In a three-necked 500 mL round-bottomed flask equipped with a thermometer, a reflux condenser under dry N_2 atmosphere, DE (1, 5.0 g) was suspended in toluene (150 mL) and vigorously stirred for 2 h at ambient temperature. CPTMS (2, 8.5 mL) was then added to the above mixture and was refluxed overnight. The resulted mixture was cooled and washed with 2-propanol (50 mL) and distilled water (2 × 50 mL), respectively. The DE-PrCl (3) was dried in a vacuum oven at 60–70 °C for 6 h.

Preparation of covalently bonded ionic liquid to the DE surfaces (DE-PrIm-Cl, 5)

A mixture of DE-PrCl (3, 2.0 g) and 1-methylimidazole (4, 0.5 mL) was suspended in toluene (100 mL) and was refluxed for 24 h. The resulting mixture was isolated by simple filtration and washed with diethyl ether (2 × 50 mL). The unreacted 1-methylimidazole was extracted with ethanol (50 mL) at 70 °C for 2 h. The solid product was filtered, was washed with diethyl ether (50 mL) and was dried in the vacuum oven at 60–70 °C for 6 h to give DE-PrIm-Cl (5).

*Preparation of immobilized ion-exchanged ionic liquids DE-PrIm-HSO_4 (**6a**) and DE-PrIm-HPW (**6b**)*

The compound 5 (1.0 g) was suspended in toluene (50 mL) with vigorous stirring in an ice bath. Sulfuric acid 98% (0.5 mL) was introduced dropwise at 0–5 °C, and then the mixture was refluxed for 48 h. The solution was cooled and completely distilled off under vacuum to remove the solvent and formed HCl from the mixture. The residue was extracted with benzene (3 × 10 mL), was dried in the vacuum oven at 60–70 °C for 6 h to produce ion-exchanged catalyst DE-PrIm-HSO_4 (**6a**). The preparation method of catalyst **6b** is similar to the abovementioned method. The compound 5 (1.0 g) was suspended in toluene (50 mL) with vigorous stirring in an ice bath. Tungstophosphoric acid (0.58 g, 0.2 mmol) was introduced step by step at 0–5 °C and then was refluxed for 48 h. The resulting mixture was distilled off under vacuum and was extracted with benzene (3 × 10 mL) and was dried in the vacuum oven at 60–70 °C for 6 h to produce ion-exchanged catalyst DE-PrIm-HPW (**6b**).

*Aza-Michael-type addition of amines to vinyl pyridine by catalysts **6a** and **6b***

In a 10 mL flask, 2-vinyl pyridine (0.53 g, 0.54 mL, 5 mmol, 1 equiv.) and aniline (0.47 g, 0.46 mL, 5 mmol, 1 equiv.) were added to a mixture of catalyst **6b** (0.1 g) in acetonitrile (5 mL) and heated for 2 h at 50 °C (Scheme 2). The progress of the

reaction was checked by TLC. After the completion of the reaction, the solid catalyst was filtered, and the solvent was evaporated. The residue was added to toluene: sodium hydroxide (33%) (1:1) biphasic system. Then the aqueous phase was extracted with dichloromethane (pH = 5.0) to remove impurities. The organic layer was evaporated, and the precipitate was washed with acetone and was dried to afford *N*-(2-(pyridin-2-yl)ethyl)aniline **7a** as a light brown solid (1.43 g, 95%). As indicated in Table 3, this reaction was performed with different amines in thermal conditions. The reaction condition of **6a** approach is similar to the procedure described above for the **6b** approach. The compound **7a** was synthesized as a light brown solid (1.25 g, 83%).

Results and discussion

In the present paper, we report the fabrication of a recoverable acidic catalyst, in which Brønsted and Lewis acids are immobilized in supported IL covalently bounded on DE surface. We also describe an efficient simple procedure for the aza-Michael-type addition of amines to vinyl pyridines using this catalytic system.

Characterization of catalyst

The X-ray diffraction patterns of DE, DE-PrIm-Cl, DE-PrIm-HSO_4 and DE-PrIm-HPW are shown in Fig. 1. XRD spectra of DE show that amorphous silica is the

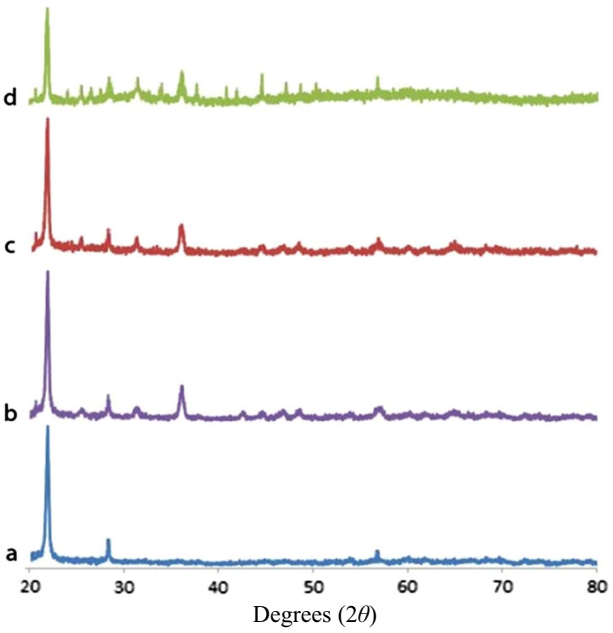


Fig. 1 XRD pattern of *a* DE; *b* DE-PrIm-Cl; *c* DE-PrIm-HSO_4 and *d* DE-PrIm-HPW

most dominant peak. The crystalline structure of compounds was characterized by XRD analysis, with representative results shown in Fig. 1. For the crystalline structure of DE, the main XRD diffractions of quartz were found at a 2θ of 22.04, 28.34 and 56.90.

Degrees (2θ)

The FT-IR spectra of the abovementioned compounds were evaluated in order to analyze the surface functional groups of the samples (Fig. 2). The broad peaks at about 1000–1100, 780 and 480 cm^{-1} in all spectra (a–e) contributed to antisymmetric stretching, symmetric stretching and bending vibrations in siloxane (Si–O–Si and Si–OH), respectively. The broad peak around 3500 cm^{-1} was related to the stretching vibrations in the structural hydroxyl groups. The presence of a peak around 2900 cm^{-1} (C–H in propyl chain) in the spectrum b indicates that the chloropropyl chain is covalently bounded to the DE surfaces with CPTMS via the

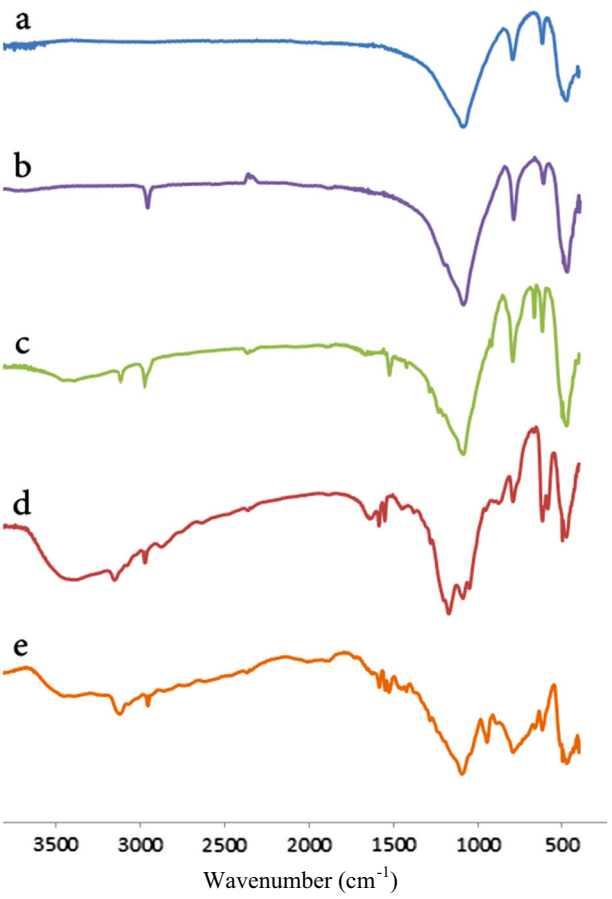


Fig. 2 FT-IR spectra of *a* DE; *b* DE-pr-Cl; *c* DE-PrIm-Cl; *d* DE-PrIm-HSO_4 and *e* DE-PrIm-HPW

method used for this work (Fig. 2b). The vibration bands of 1-methylimidazole and propyl chain in the DE-PrIm-Cl suggest that ionic liquid 1-methylimidazolium chloride (1600 cm^{-1}, imidazole ring) was successfully loaded on the DE surfaces (Fig. 2c). The FT-IR spectra of compounds DE-PrIm-HSO_4 and DE-PrIm-HPW indicate that sulfate anion (1350–1450 cm^{-1}, S=O in sulfate ion) and anionic polytungstatophosphate (800–1000 cm^{-1}, Keggin type heteropolyanions) were successfully exchanged with chloride anion in the catalytic system (Fig. 2d, e).

Wave number (cm^{-1})

The thermal stability of DE, DE-PrCl, DE-PrIm-Cl, DE-PrIm-HSO_4 and DE-PrIm-HPW was evaluated by thermogravimetric analysis (TGA) curves (Fig. 3). The TGA curves show the mass loss of the organic materials as they decompose with an increase in heating. The first mass loss at 25–100 °C contributes to the evaporation of physically adsorbed water. The second mass loss at 200–400 °C is related to the thermal decomposition of organochloropropyl fragments covalently bonded to the DE surfaces. In the case of DE-PrIm-HSO_4 (Fig. 1a), the further mass loss contributes to the thermal decomposition in the presence of acidic HSO_4.

The SEM images of natural DE and functionalized DE are displayed in Fig. 4, showing there has been a little change in the average particle size.

The specific surface areas of particles were determined using standard BET (Brunauer–Emmett–Teller) techniques. The BET surface area and the pore diameter of DE were determined as a moderate surface area for the catalytic application. The mean pore diameter and pore volume of the DE particles were 16.33 nm and 0.0028 cm^3/g, respectively. The BET specific surface area, pore diameter, and volume of functionalized DE particles were fairly similar to DE. As shown in

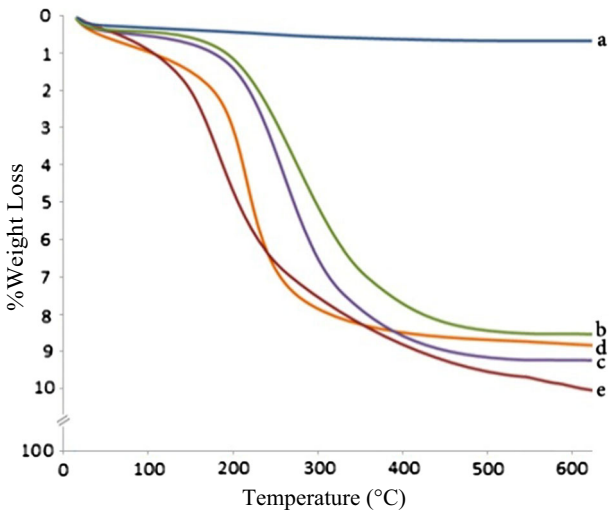


Fig. 3 TGA thermograms of *a* DE; *b* DE-pr-Cl; *c* DE-PrIm-Cl; *d* DE-PrIm-HPW and *e* DE-PrIm-HSO_4

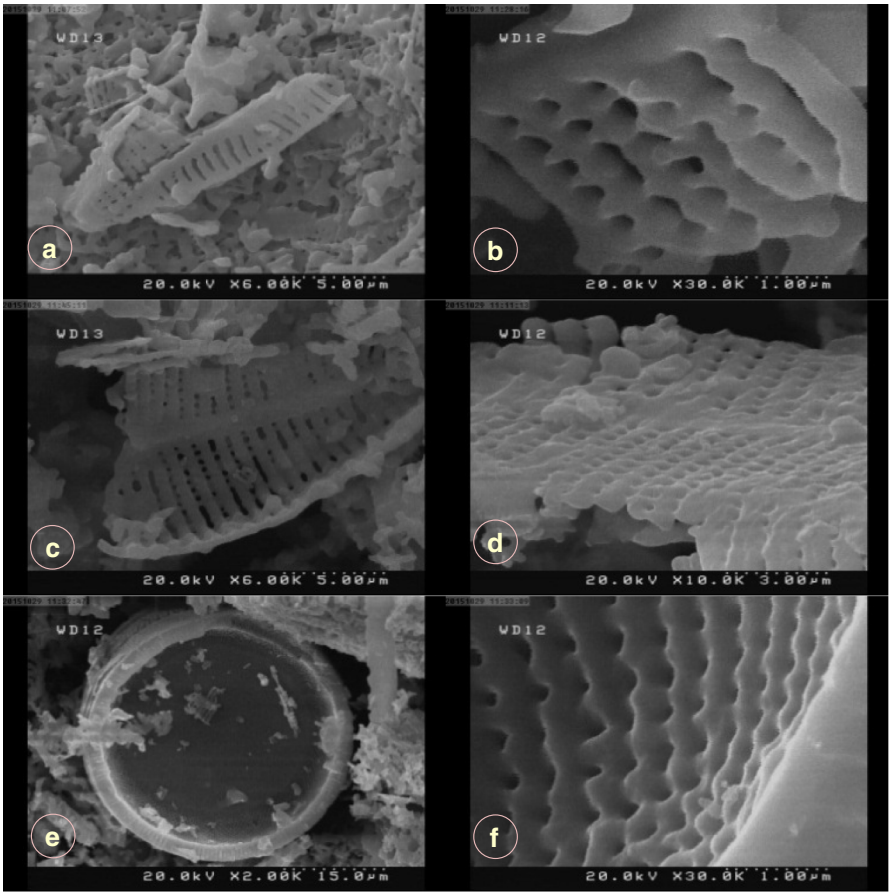


Fig. 4 SEM images of **a** DE; **b** DE-pr-Cl; **c** DE-PrIm-Cl; **d** DE-PrIm-HSO_4, **e** and **f** DE-PrIm-HPW

Table 1 Textural properties of DE, DE-PrIm-HSO_4, DE-PrIm-HPW

Material	S_{BET} (m^2/g)	Mean pore diameter (nm)	Total pore volume (cm^3/g)
DE	0.70	16.33	0.0028
DE-PrIm-HSO_4	2.83	25.66	0.018
DE-PrIm-HPW	2.50	23.23	0.014

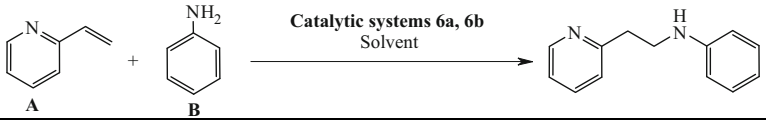
Table 1, functionalization of DE with CPTMS leads to increased surface area and pore volume in DE-PrIm-HSO_4 and DE-PrIm-HPW, respectively. The higher surface areas of DE-PrIm-HSO_4 and DE-PrIm-HPW can be attributed to the more adsorption of N_2 gasses by functionalized groups on the immobilized catalyst on the support. The presence of organic molecules contributing the nitrogen absorption on

the support pore surfaces resulted in more complexity and increased nitrogen absorption and thereby increased surface area.

Effect of anion-exchanged catalytic system 6a and 6b

The anion-exchange step was carried out using sulfuric acid and tungstophosphoric acid (Scheme 1). As illustrated in Table 2, the best results are obtained using anionic polyoxometalates as the catalytic system. Employing anionic polyoxometalates as inorganic compounds with high crystal lattice energies in supported ionic liquids effectively increases their application as the catalyst in organic synthesis. Polyoxometalates possess powerful Brønsted acidity, even stronger than conventional Brønsted acids such as H_2SO_4, and conventional Lewis acids. Polyoxometalates show excellent catalytic activity, specifically in acid-catalyzed reactions, including aza-Michael-type addition as described throughout this paper. Among the polyoxometalates used in this paper, phosphotungstic acid HPW was found to be a highly effective anion-exchanged catalyst for the abovementioned reactions. Polyoxometalates are generally more efficient proton donors than ordinary acids; consequently, they are stronger catalysts. Additionally, anionic polyoxometalates can stabilize intermediates in organic reactions and substantially have an important function in the reaction catalysis [37]. Phosphotungstic acid

Table 2 Aza-Michael-type addition of aniline to 2-vinylpyridine catalyzed by catalytic systems **6a** and **6b**[a]



A **B**

Entry	Catalytic system		Solvent	Mole ratio (A:B)	Time (h)	Yield (%)[b]
1	DE		CH_3CN	1:1	1	Trace
2	H_2SO_4		CH_3CN	1:1	1	45
3	$H_3PW_{12}O_{40}$		CH_3CN	1:1	1	72
4	DE-PrIm-HSO_4	**6a**	CH_3CN	1:1	1	83
5	DE-PrIm-HPW	**6b**	CH_3CN	1:1	1	90
6	DE-PrIm-HPW	**6b**	CH_3CN	1:1	2	95
7	DE-PrIm-HPW	**6b**	CH_3CN	1:2	2	95
8	DE-PrIm-HPW	**6b**	CH_3CN	1:1	2	70[c]
9	DE-PrIm-HPW	**6b**	THF	1:1	2	75
10	DE-PrIm-HPW	**6b**	DMF	1:1	2	73
11	DE-PrIm-HPW	**6b**	H_2O	1:1	2	82
12	DE-PrIm-HPW	**6b**	CH_2Cl_2	1:1	2	60

[a] Reactions conditions: vinyl pyridine (5 mmol, 1 equiv.), aniline (5 mmol, 1 equiv.), solvent (5 mL), catalyst (0.1 g), 50 °C

[b] Isolated yield

[c] The reaction was performed at room temperature

HPW is the preferred acid catalyst compared to other polyoxometalates used in this paper due to its stronger acidity, higher hydrolytic and thermal stability, and decreased oxidation potentials.

Effect of catalytic system 6a and 6b on aza-Michael-type addition

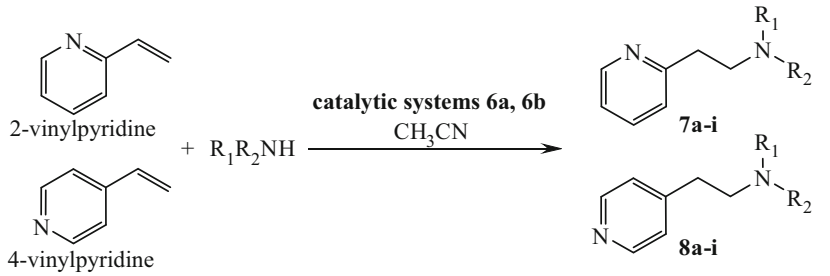
Using DE as a heterogeneous support without any acidic catalysts was accompanied with poor results (Table 2, Entry 1). Among various particles as heterogeneous solid supports, **6b** is an efficient and recoverable catalyst in the organic reactions described here. Because of dual catalytic action in HPAs (Brønsted and Lewis acid), **6b** acts as an extraordinary catalyst. Considering the reaction efficiency and catalyst recyclability, the use of **6b** and **6a** as the catalyst shows the better results compared with the use of phosphotungstic acid and sulfuric acid, respectively. So, the catalytic performances of the catalytic systems **6b** and **6a** were higher than for the corresponding use of phosphotungstic acid (Table 2, entries 3 and 5) and sulfuric acid individually (Table 2, entries 2 and 4). Due to improved results through the use of **6b** as a recoverable catalyst, some more experiments were performed by changing the reaction conditions such as reaction time (Table 2, Entry 6), the molar ratio of reactants (Table 2, Entry 7), reaction temperature (Table 2, Entry 8) and solvents (Table 2, entries 9–12). The best results were obtained using **6b** as catalyst (0.1 g) in acetonitrile as a polar solvent (5 mL) for 2 h at 50 °C (Table 2, Entry 6). To evaluate the catalytic performance of **6b** and its repeatability as Brønsted and Lewis acids, more experiments were examined comparing the catalytic system **6a** as Brønsted acid only (Table 3, Fig. 5). In the absence of the catalytic system, the transformations did not occur because of the activation barrier (Table 3, entry 10).

The products are easily separated in increased yields and high purity by simple purification of the precipitated solid after evaporation of the solvent. The work-up procedure involves simple filtration of catalytic particles and evaporation of the organic solvent.

The mechanistic aspects

The addition reaction between amine and vinyl pyridine follows the aza-Michael-type mechanism (Fig. 6a). The aza-Michael reaction is due to the nucleophilic attack of a primary and/or secondary amine ***i*** to an activated vinyl compound ***ii***. In the case of 2-vinyl pyridine and 4-vinyl pyridine, the aza-Michael addition occurs at the 1,4- and 1,6-position, respectively. The vinyl compound can be activated via H-bond interaction between a nitrogen atom in the pyridine ring and the protons in acidic heterogeneous catalysts **6a** and **6b**. Additionally, the vinyl compound is more activated by the interaction between a nitrogen atom in the pyridine ring and Lewis acidic sites, using catalyst **6b**. The transition state **ILTS** thus obtained is well stabilized through the polar interaction of anionic pyridinium and cationic imidazolium in supported ionic liquid (Fig. 6b).

Table 3 Aza-Michael-type addition of amines to 2-vinylpyridine and 4-vinylpyridine catalyzed by catalysts **6a** and **6b**[a]



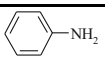
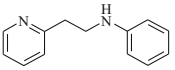
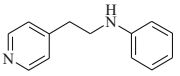
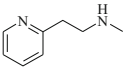
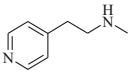
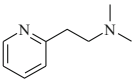
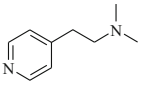
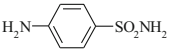
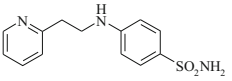
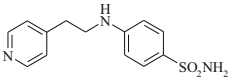
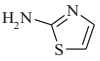
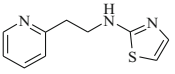
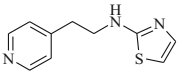
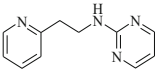
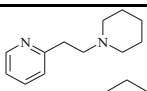
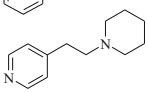
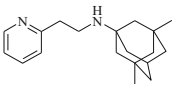
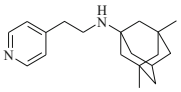
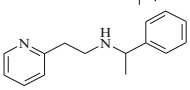
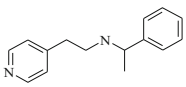
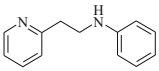
Entry	Amine	Product		Yield (%)[b]	
				6a	**6b**
1			**7a**	83	95
			**8a**	90	98
2	CH_3NH_2 (%40, aq)		**7b**	78	90
			**8b**	80	93
3	Me_2NH		**7c**	81	95
			**8c**	75	89
4			**7d**	73	95
			**8d**	63	90
5			**7e**	71	85
			**8e**	68	94
6			**7f**	74	93

Table 3 continued

Entry	Amine	Product		Yield (%)[b]	
				6a	**6b**
7			**7g**	70	90
			**8g**	86	95
8			**7h**	63	82
			**8h**	71	90
9			**7i**	68	80
			**8i**	75	88
10			**7a**	Trace[c]	Trace[c]

[a] Reactions conditions: vinyl pyridine (5 mmol, 1 equiv.), amine (5 mmol, 1 equiv.), acetonitrile (5 mL), catalyst (0.1 g), 50 °C, 2 h

[b] Isolated yield

[c] The reaction was performed without any catalyst

Recyclability of the catalytic system

Catalyst recyclability is one of the most important features in heterogeneous catalysts. The catalytic system was successfully recycled five times without any remarkable loss of its catalytic activity (Fig. 7). At the end of each reaction, the catalytic system was separated by a simple filtration and carefully was washed twice with ethanol, and then was reused as a catalyst for the next reaction under the same conditions. After reuse five times, the recycled catalysts **6b** maintained their efficiency. The structure and activity of **6b** catalyst remained constant during the reaction conditions.

Experimental data

To make reading more convenient, NMR analysis data of selected entries is provided here.

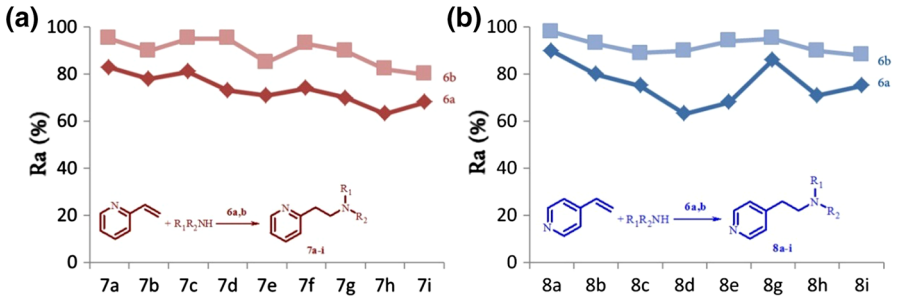


Fig. 5 Comparisons of catalytic activity between catalysts **6a** and **6b** on aza-Michael-type addition starting with **a** 2-vinylpyridine and **b** 4-vinylpyridine

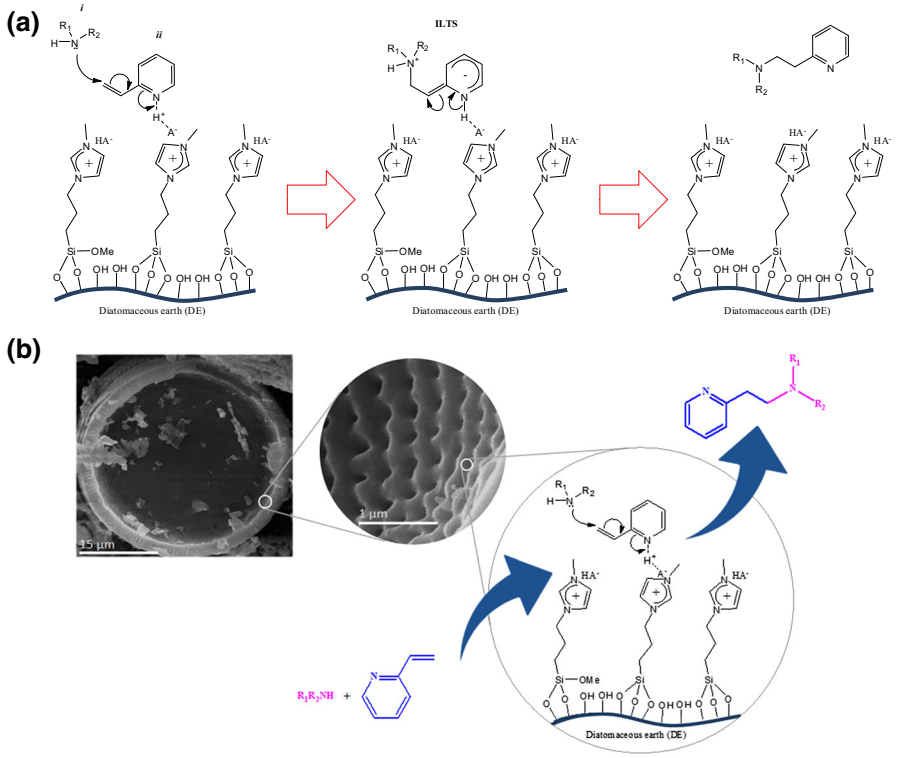


Fig. 6 The plausible mechanism for activation of 2-vinyl pyridine by DE-PrIm-HA$^-$ catalytic system

*N-(2-(pyridin-2-yl)ethyl)aniline (**7a**)*

$C_{13}H_{14}N_2$; mp: 40–43 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 3.09 (t, 2H, J = 6.6 Hz), 3.54 (b, 2H), 4.30 (b, 1H), 6.67 (*d*, 2H, J = 7.6 Hz), 6.74 (*t*, 1H, J = 7.2 Hz), 7.12 (t, 2H, J = 6.0 Hz), 7.21 (t, 2H, J = 7.5 Hz), 7.57 (t, 1H, J = 6 Hz), 8.57 (d, 1H, J = 4.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm): 37.4, 43.5,

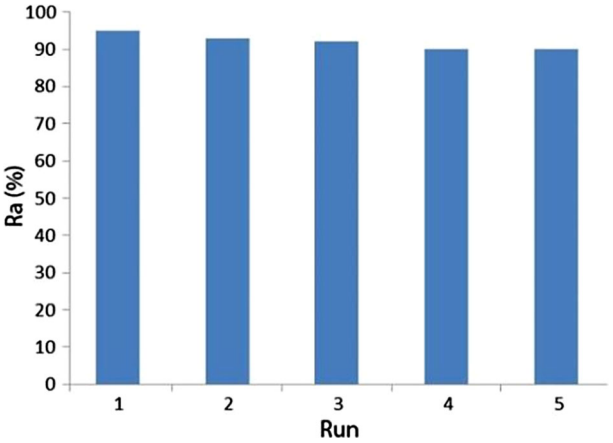


Fig. 7 Recyclability of the catalytic system **6b** for the reaction of 2-vinylpyridine with aniline

112.9, 117.2, 121.5, 123.4, 129.3, 136.6, 148.3, 149.3, 159.8; IR $\bar{\upsilon}(cm^{-1})$: 685, 959, 1273, 1437, 1478, 1601, 1696, 2930, 3067, 3411; MS (M^+, *m/z*): 198; Anal. Calcd: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.92; H, 7.01; N, 14.05.

N-(2-(pyridin-4-yl)ethyl)aniline ***(8a)***

$C_{13}H_{14}N_2$; mp: 43 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 3.03 (t, 2H, $J = 7.2$ Hz), 3.60 (t, 2H, $J = 6.8$ Hz), 7.05–7.27 (m, 5H), 8.49–8.55 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 33.3, 45.3, 113.3, 121.2, 123.2, 129.6, 150.3, 160.6, 160.7; IR $\bar{\upsilon}(cm^{-1})$: 603, 690, 998, 1148, 1215, 1437, 1492, 1601, 1696, 2936, 3057, 3242; Anal. Calcd: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.61; H, 7.23; N, 14.16.

N-methyl-2-(pyridin-2-yl)ethanamine ***(7b)***

$C_8H_{12}N_2$; viscous yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 2.57 (s, 3H), 3.43 (t, 2H, $J = 5.2$ Hz), 3.56 (t, 2H, $J = 6.8$ Hz), 7.96 (t, 1H, $J = 6.4$ Hz), 8.08 (d, 1H, $J = 8.0$ Hz), 8.55 (t, 1H, $J = 8.0$ Hz), 8.85 (d, 1H, $J = 5.6$ Hz), 9.62 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 29.5, 32.6, 46.6, 126.0, 128.1, 142.3, 146.4, 152.6; IR $\bar{\upsilon}(cm^{-1})$: 590, 999, 1109, 1418, 1604, 1656, 2850, 2938, 3030, 3462; Anal. Calcd: C, 70.55; H, 8.88; N, 20.57. Found: C, 70.57; H, 8.76; N, 20.63.

N-methyl-2-(pyridin-4-yl)ethanamine ***(8b)***

$C_8H_{12}N_2$; viscous yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 2.36 (s, 3H), 2.61–2.78 (m, 4H), 5.27 (bs, 1H), 7.00–7.06 (m, 2H), 8.38–8.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 35.4, 36.2, 51.9, 124.1, 149.4, 149.5; IR $\bar{\upsilon}(cm^{-1})$: 591,

812, 996, 1110, 1413, 1607, 2854, 2948, 3035, 3442; MS (M^+, *m/z*): 135; Anal. Calcd: C, 70.55; H, 8.88; N, 20.57. Found: C, 70.65; H, 8.92; N, 20.46.

*N,N-dimethyl-2-(pyridin-2-yl)ethanamine (**7c**)*

$C_9H_{14}N_2$; viscous yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 2.40 (s, 6H), 3.54 (t, 2H, $J = 7.6$ Hz), 3.80 (t, 2H, $J = 7.6$ Hz), 7.56 (d, 1H, $J = 10.4$ Hz), 7.60 (d, 1H, $J = 7.6$ Hz), 8.64 (t, 1H, $J = 7.6$ Hz), 8.85 (d, 1H, $J = 6.4$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 41.2, 45.2, 58.1, 121.5, 125.7, 136.1, 148.5, 156.4; IR $\bar{\upsilon}$ (cm^{-1}): 590, 1001, 1264, 1419, 1464, 1604, 2820, 2948; Anal. Calcd: C, 71.96; H, 9.39; N, 18.65. Found: C, 72.09; H, 9.31; N, 18.63.

*N,N-dimethyl-2-(pyridin-4-yl)ethanamine (**8c**)*

$C_9H_{14}N_2$; viscous yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 2.27 (s, 6H), 2.54 (t, 2H, $J = 7.6$ Hz), 2.75 (t, 2H, $J = 8.0$ Hz), 7.11 (d, 2H, $J = 4.0$ Hz), 8.46 (d, 2H, $J = 2.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 33.4, 45.3, 60.0, 124.1, 149.5, 149.6; IR $\bar{\upsilon}$(cm^{-1}): 591, 1001, 1220, 1419, 1464, 1604, 1645, 2778, 2947, 3029; MS (M^+, *m/z*): 149; Anal. Calcd: C, 71.96; H, 9.39; N, 18.65. Found: C, 72.05; H, 9.31; N, 18.59.

*4-(2-(pyridin-2-yl)ethylamino)benzenesulfonamide (**7d**)*

$C_{13}H_{15}N_3O_2S$; mp: 122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 3.10 (t, 2H, $J = 6.3$ Hz), 3.59 (t, 2H, $J = 6.6$ Hz), 4.59 (bs, 2H, NH_2), 5.00 (bs, 1H), 6.62 (d, 2H, $J = 9.0$ Hz), 7.16–7.27 (m, 2H), 7.6–7.7 (m, 3H), 8.57 (d, 1H, $J = 3.6$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm): 38.0, 44.6, 111.7, 118.2, 121.5, 123.4, 129.3, 137.8, 157.1, 162.3, 177.0; IR $\bar{\upsilon}$(cm^{-1}): 600, 1003, 1143, 1299, 1423, 1599, 1734, 2861, 2930, 3335; MS (M^+, *m/z*): 277; Anal. Calcd: C, 56.30; H, 5.45; N, 15.15. Found: C, 56.42; H, 5.51; N, 15.17.

*4-(2-(pyridin-4-yl)ethylamino)benzenesulfonamide (**8d**)*

$C_{13}H_{15}N_3O_2S$; mp: 167–169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 3.41 (t, 2H, $J = 8.8$ Hz), 4.40 (t, 2H, $J = 8.8$ Hz), 6.63–6.70 (m, 2H), 7.10–7.34 (m, 4H), 8.45–8.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 36.7, 42.7, 109.3, 124.0, 128.1, 130.4, 148.2, 150.7, 156.7; IR $\bar{\upsilon}$(cm^{-1}): 600, 826, 1003, 1143, 1299, 1422, 1598, 1730, 2861, 2930, 3364, 3465; Anal. Calcd: C, 56.30; H, 5.45; N, 15.15. Found: C, 56.42; H, 5.51; N, 15.22.

*N-(2-(pyridin-2-yl)ethyl)thiazol-2-amine (**7e**)*

$C_{10}H_{11}N_3S$; mp: 145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 3.16 (t, 2H, $J = 6.8$ Hz), 4.07 (t, 2H, $J = 6.4$ Hz), 5.65 (d, 1H, $J = 4.0$ Hz), 6.18 (d, 1H, $J = 3.6$ Hz), 7.12 (m, 2H), 7.60 (m, 1H), 8.52 (d, 1H, $J = 3.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 36.2, 45.7, 97.0, 121.7, 123.9, 136.7, 139.1, 149.3,

158.2, 164.3; IR $\bar{\upsilon}$(cm^{-1}): 752, 994, 1110, 1265, 1320, 1418, 1504, 1601, 2862, 2932, 3030, 3332; MS (M^+, *m/z*): 205; Anal. Calcd: C, 58.51; H, 5.40; N, 20.47. Found: C, 58.55; H, 5.53; N, 20.58.

*N-(2-(pyridin-4-yl)ethyl)thiazol-2-amine (**8e**)*

$C_{10}H_{11}N_3S$; mp: 177–179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 2.94 (t, 2H, $J = 6.8$ Hz), 3.46 (t, 2H, $J = 7.2$ Hz), 6.64–6.80 (m, 2H), 7.10–7.30 (m, 2H), 8.52–8.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 34.9, 44.0, 113.0, 117.8, 124.2, 129.3, 129.4, 150.1; IR $\bar{\upsilon}$(cm^{-1}): 694, 752, 995, 1110, 1418, 1504, 1601, 2862, 2932, 3029, 3332; Anal. Calcd: C, 58.51; H, 5.40; N, 20.47. Found: C, 58.92; H, 5.43; N, 20.56.

*N-(2-(pyridin-2-yl)ethyl)pyrimidin-2-amine (**7f**)*

$C_{11}H_{12}N_4$; mp: 195–199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 3.08 (t, 2H, $J = 6.4$ Hz), 3.80 (t, 2H, $J = 6.4$ Hz), 7.08–7.13 (m, 2H), 7.60 (t, 1H, $J = 4.4$ Hz), 7.72–7.83 (m, 2H), 8.71 (s, 2H), 8.91–8.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 37.5, 40.9, 111.4, 121.2, 122.4, 136.5, 149.4, 155.7, 158.0, 159.5; IR $\bar{\upsilon}$ (cm^{-1}): 994, 1149, 1413, 1474, 1590, 1645, 2936, 3178, 3352; MS (M^+, *m/z*): 200; Anal. Calcd: C, 65.98; H, 6.04; N, 27.98. Found: C, 66.09; H, 5.90; N, 27.88.

*2-(2-(piperidin-1-yl)ethyl)pyridine (**7g**)*

$C_{12}H_{18}N_2$; viscous yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 1.39–1.63 (m, 6H), 2.44 (m, 4H), 2.67 (t, 2H, $J = 8.0$ Hz), 2.94 (t, 2H, $J = 7.6$ Hz), 7.50–7.53 (m, 2H), 8.46 (d, 1H, $J = 4.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 24.3, 27.0, 31.4, 53.0, 54.5, 122.8, 124.2, 134.0, 150.1, 153.5; IR $\bar{\upsilon}$(cm^{-1}): 554, 765, 994, 1116, 1436, 1590, 2940; MS (M^+, *m/z*): 190; Anal. Calcd: C, 75.74; H, 9.53; N, 14.72. Found: C, 75.61; H, 10.59; N, 14.75.

*4-(2-(piperidin-1-yl)ethyl)pyridine (**8g**)*

$C_{12}H_{18}N_2$; viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 1.59 (m, 6H), 2.42 (m, 4H), 2.53 (t, 2H, $J = 8.0$ Hz), 2.71 (t, 2H, $J = 8.4$ Hz), 7.10 (d, 2H, $J = 4.4$ Hz), 8.45 (t, 2H, $J = 2.4$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 24.3, 25.9, 32.9, 54.5, 59.9, 124.2, 149.6, 149.7; IR $\bar{\upsilon}$(cm^{-1}): 759, 992, 1110, 1274, 1437, 1478, 1601, 1696, 2930, 3069; Anal. Calcd: C, 75.74; H, 9.53; N, 14.72. Found: C, 75.69; H, 9.43; N, 14.77.

*N-(3,5-Dimethyl-adamantan-1-yl)-2-(pyridin-2-yl)ethanamine (**7h**)*

$C_{19}H_{28}N_2$; mp: 196–198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 1.09 (s, 6H), 1.20 (s, 3H), 1.26 (m, 6H), 1.42 (s, 3H), 2.10 (s, 1H), 3.64 (t, 2H, $J = 9.2$ Hz), 4.17 (t, 2H, $J = 7.6$ Hz), 7.33 (d, 2H, $J = 7.6$ Hz), 8.56 (t, 2H, $J = 2.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 30.1, 30.5, 32.6, 42.6, 42.9, 44.6, 49.1, 50.6, 52.3, 121.2, 122.4,

136.5, 149.5, 155.7; IR $\bar{\upsilon}(cm^{-1})$: 803, 990, 1053, 1453, 1587, 1739, 2840, 2901, 2942, 3436; MS (M^+, *m/z*): 284; Anal. Calcd: C, 80.23; H, 9.92; N, 9.85. Found: C, 80.09; H, 10.01; N, 9.90.

*N-(3,5-Dimethyl-adamantan-1-yl)-2-(pyridin-4-yl)ethanamine (**8h**)*

$C_{19}H_{28}N_2$; mp: 210–214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 0.93 (s, 6H), 1.29 (s, 3H), 1.42 (m, 6H), 1.44 (s, 3H), 2.10 (s, 1H), 3.94 (t, 2H, $J = 8.4$ Hz), 4.20 (t, 2H, $J = 9.2$ Hz), 7.25 (d, 2H, $J = 6.0$ Hz), 8.54 (d, 2H, $J = 6.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 30.5, 32.4, 32.6, 42.6, 42.9, 44.5, 49.1, 50.5, 52.3, 124.1, 149.7, 150.1; IR $\bar{\upsilon}(cm^{-1})$: 779, 994, 1049, 1474, 1590, 1645, 2936, 3351; MS (M^+, *m/z*): 284; Anal. Calcd: C, 80.23; H, 9.92; N, 9.85. Found: C, 80.26; H, 9.88; N, 9.79.

*1-phenyl-N-(2-(pyridin-2-yl)ethyl)ethanamine (**7i**)*

$C_{15}H_{18}N_2$; mp: 233–235 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 1.41 (s, 3H), 2.94 (m, 1H), 3.83 (t, 2H, $J = 6.8$ Hz), 4.12 (t, 2H, $J = 6.4$ Hz), 7.05–7.58 (m, 7H), 8.52 (d, 2H, $J = 4.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 24.4, 37.3, 47.3, 58.3, 115.4, 119.3, 126.9, 128.4, 128.5, 145.5, 149.2, 149.5, 160.4; IR $\bar{\upsilon}(cm^{-1})$: 590, 761, 995, 1122, 1449, 1591, 2865, 2964, 3025, 3060, 3366; MS (M^+, *m/z*): 226; Anal. Calcd: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.68; H, 8.12; N, 12.05.

Conclusions

Catalysis with anionic polyoxometalate is an excellent choice with growing importance. The properly investigated organic transformations in this paper clearly show the extensive range of hopeful applications of anionic polyoxometalate in supported ionic liquid phase. Anionic polyoxometalate requires higher activity and selectivity with cleaner processing. The high efficiency of polyoxometalate as an acid catalyst is due to their extreme Brønsted acidity, which is stronger than conventional mineral acids.

In conclusion, the method for some useful organic transformations using a heterogeneous anion-exchanged supported ionic liquid catalyst, as reported in this paper, is an efficient and mild procedure with simple work-up. The aza-Michael-type addition of amines to vinyl pyridine using catalytic systems **6a** and **6b** as efficient and recoverable catalysts was successfully examined in this article. The best results were achieved using **6b** as an excellent reproducible catalyst. We prepared two supported ionic liquids **6a** and **6b** and mainly focused on the use of **6b** in the abovementioned reactions. This catalytic system is immiscible with the reaction mixture; consequently, at the end of the reaction, the solid catalyst can be easily separated from the reaction mixture. Product isolation involves simple separation of the solid catalyst followed by purification of residue. Therefore, the advantages of homogeneous and heterogeneous catalysis can be successfully integrated, which greatly facilitate recovery and recycling of the catalyst. This

method is a useful alternative to other methods in the literature. The reactions are usually carried out under mild conditions with elevated yields and simple work-up. The catalytic system can be easily separated from the reaction mixture and recycled in subsequent reactions.

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