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四乙烯五胺功能化酚醛树脂作为 Knoevenagel 缩合反应的高活性酸碱双功能催化剂

肖 剑 武志英 陈姿依 赵朋飞 刘春艳*
(华北理工大学药学院 河北唐山 063210)

摘要 通过市售酚醛树脂(PR)和四乙烯五胺经由氨化反应制备四乙烯五胺官能化酚醛树脂(TEPA-PR), 并应用于催化 Knoevenagel 缩合反应. 通过傅里叶转移红外光谱(FTIR)、X 射线衍射光谱(XRD)和元素分析(EA)表征 TEPA-PR 结构. TEPA-PR 可高效催化芳香醛的 Knoevenagel 缩合反应, 具有产率高, 底物适用性广的优势. 此外, 该反应可在不同极性溶剂中进行. 该新型树脂催化剂表现出良好的可循环使用性, 使用 5 次后其催化活性没有显着降低.
关键词 酚醛树脂; 酸碱催化; 多相催化; Knoevenagel 缩合反应; 水相催化

Tetraethylenepentamine Functionalized Phenolic Resin as Highly Active Acid-Base Bifunctional Catalyst for Knoevenagel Condensation Reaction

Xiao, JIan Wu, Zhiying Chen, Ziyi Zhao, Pengfei Liu, Chunyan*
(*College of Pharmacy*, *North China University of Science and Technology*, *Tangshan*, *Hebei 063210*)

Abstract The tetraethylenepentamine functionalized phenolic resin (TEPA-PR) for Knoevenagel condensation reaction has been prepared by aminating a commercially available phenolic resin (PR) and tetraethylenepentamine. The TEPA-PR was characterized by Fourier-transfer infrared spectroscopy (FTIR), X-ray diffraction spectra (XRD) and elemental analysis (EA). The TEPA-PR can efficiently catalyze Knoevenagel condensation reaction of aromatic aldehydes with high yields of a wide range of products. Furthermore, the reaction can be easily carried out in different solvents of different polarity. The novel developed resin catalyst shows good reusability (5 times) without significant decrease of catalytic activity.
Keywords phenolic resin; acid-base catalysis; heterogeneous catalysis; Knoevenagel condensation reaction; water phase catalysis

1 Introduction

Knoevenagel condensation reaction was widely used in chemical industry for the synthesis of *α,β*-unsaturated carbonyl compounds.[1] Due to its important synthetic value, various catalysts have been developed for this reaction, and some of them have good catalytic activity.[2] However, most of these reaction systems have some disadvantages, such as use of non-reusable catalysts, long reaction time, high reaction temperature as well as the use of toxic solvents.[3] Therefore, preparation of newly catalysts for Knoevenagel condensation reaction has research significance.

Recently, many efforts have been made to prepare heterogeneous catalysts through using various support materials, including SiO_2,[4] SBA-15,[5] MCM-41,[6] GO,[7] polymers,[8] magnetic Fe_3O_4,[9] and MOFs.[10] These heterogeneous catalysts have some advantages, such as high efficiency and simple post-treatment steps. However, many of them are difficult to use multiple times, and the reaction medium is mainly limited to organic solvent. Therefore, preparation of novel heterogeneous catalysts has high research value.

Phenolic Resin (PR), a synthetic resin, has many advantages of low cost, high temperature resistance, good corrosion and mildew resistant, excellent mechanical strength and stability, and good chemical stability. Moreover, the PR contains an abundance of phenolic hydroxyl groups which can be easily modified various target func-

* Corresponding author. E-mail: chunyanliu@ncst.edu.cn
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tional groups. Therefore, the PR should be a suitable support for the preparation of a heterogeneous catalyst. In this work, the bromopropyl functionalized phenolic resin (Br-PR) was prepared by nucleophilic substitution reaction of PR and 1,3-dibromopropane. The tetraethylenepentamine functionalized phenolic resin (TEPA-PR) was then prepared through nucleophilic substitution reaction of Br-PR and tetraethylenepentamine. The structures of the TEPA-PR were shown in Scheme 1. The catalytic activity of the TEPA-PR was detected, and the TEPA-PR was characterized as follow.

2 Results and discussion

2.1 Characterization of PR-immobilized TEPA catalysts.

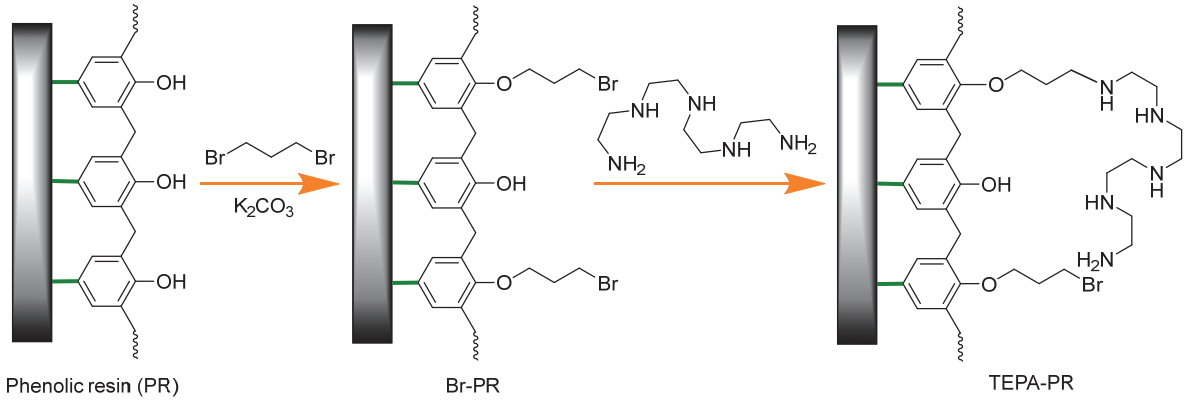
The TEPA functionalized resins with different functionality were determined to verify the successful preparation of these organic base catalysts. The amino contents of the different resins were tested using acid-base titrations. The results are shown in Table 1, indicating that the TEPA moieties have been efficiently immobilized in resin.

Fourier transform infrared spectroscopy (FTIR) was used to determine the resins structures. The FTIR spectra of PR, Br-PR and TEPA-PR are shown in the Figure 1. The strong adsorption peak at 3300 cm^{-1} was owned to the stretching vibration of O—H in phenolic hydroxyl. The adsorption peaks at 842 and 752 cm^{-1} are attributed to out-of-plane bending vibrations of the benzene rings. Compared with PR, the adsorption peaks of O—H and benzene rings in the functionalized resins were weakened, showing that the introduction of the target segment during the loading process reduces the relative proportion of the original groups (curve a). The original resin has an adsorption peak at 2930 cm^{-1}, which is attributed to the stretching vibration of C—H in methylene. After modification, the adsorption peak of methylene in the Br-PR and the TEPA-PR strengthen obviously, indicating that the moieties of $CH_2CH_2CH_2Br$ and TEPA were successfully modified into resin (curves b, c).

Table 1 Amino and TEPA content of the TEPA-functionalized PR

Entry	Resin	Amino content/ (mmol•g^{-1})	TEPA content/ (mmol•g^{-1})
1	TEPA-PR	4.875	0.975
2	TEPA-PR-1	3.085	0.617
3	TEPA-PR-2	1.625	0.325

The X-ray diffraction (XRD) can observe the crystal structure of the resins, and the XRD spectra of PR are shown in Figure 2. Compared with original PR, the XRD spectra of the functionalized resins Br-PR and TEPA-PR have changed significantly, suggesting that the crystal structure of the functionalized resin has changed greatly during the loading process.



Scheme 1 Tetraethylenepentamine-immobilized PANF catalysts

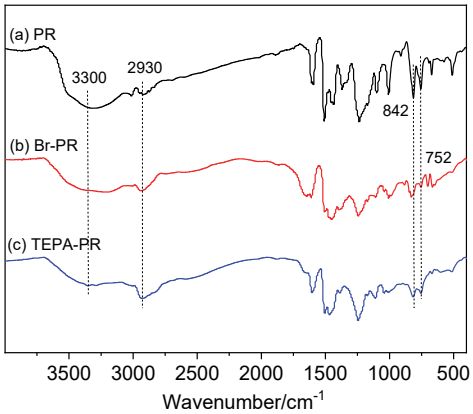


Figure 1 FTIR spectra of (a) PR, (b) Br-PR and (c) TEPA-PR

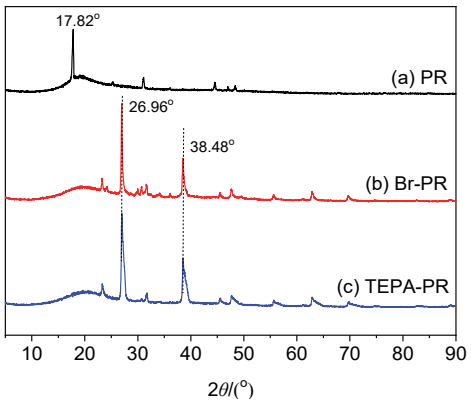


Figure 2 XRD spectra of (a) PR, (b) Br-PR and (c) TEPA-PR

The X-ray photoelectron spectroscopy (XPS) was applied to test the chemical properties of the TEPA-PR. The result is shown in Figure 3. The peaks at 70.2 and 67.8 eV correspond to the binding energy of Br 3d, proving that some unreacted bromopropyl remains in the catalyst TEPA-PR (Figure 3a). Additionally, the corresponding N 1s spectrum of the TEPA-PR has the peaks at 401.2 and 399.2 eV, which can be attributed to the N—H and C—N bonds in the TEPA-PR (Figure 3b). Furthermore, there are three peaks at 288.3, 286.0 and 284.4 eV corresponding to C 1s XPS spectrum of the TEPA-PR, which can be owned to the C—O, C—H and C—N bonds in the TEPA-PR, respectively (Figure 3c). Moreover, the peaks at 533.1 and 532.0 eV were attributed to the O 1s in the TEPA-PR (Figure 3d). XPS spectra further proves the successfully preparation of the TEPA-PR.[11]

The elemental analysis (EA) was used to detect the composition of elements of functionalized resins, and the EA data of the Br-PR and the TEPA-PR are shown in Table 2. Compared with the Br-PR, the TEPA-PR has higher C, H and N contents, the reason is that the modified TEPA moiety has higher C, H and N content (Entries 1, 2). EA data proves that resin has been successfully immobilized. The functionality of the TEPA-PR calculated by N content of EA is about 0.807 mmol/g.

Table 2 Elemental analysis data

Entry	Resin	Elemental analysis		
		N	C	H
1	Br-PR	1.728	55.713	5.114
2	TEPA-PR	5.647	60.506	5.264

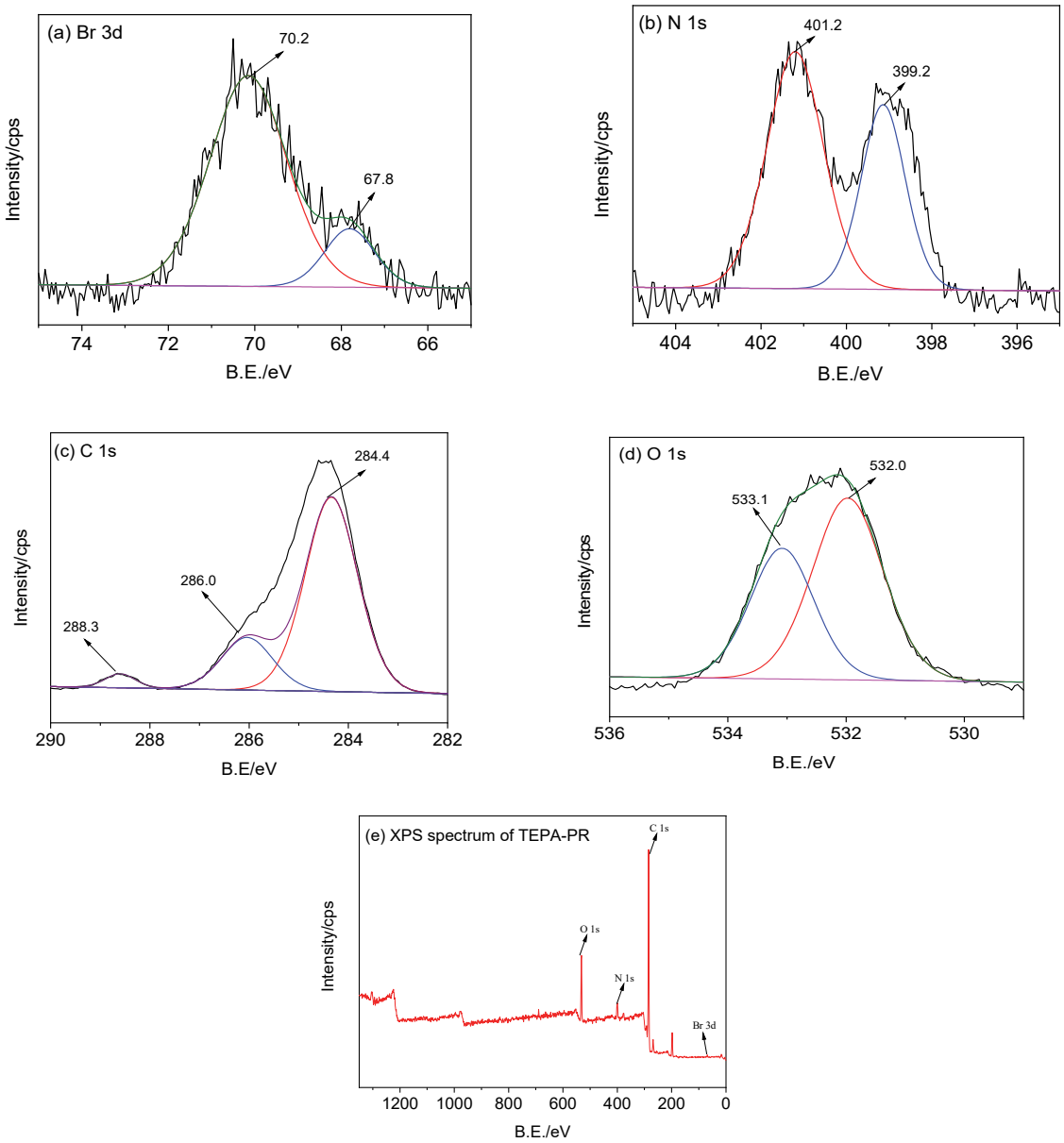


Figure 3 (a) Br 3d spectra of the TEPA-PR, (b) N 1s spectra of the TEPA-PR, (c) C 1s spectra of the TEPA-PR, (d) O 1s spectra of the TEPA-PR and (e) XPS survey spectrum of the TEPA-PR

2.2 Catalytic activity of the TEPA-PR

2.2.1 Catalyst activity of the TEPA-PR

The catalyst TEPA-PR was used to catalyze the Knoevenagel condensation reaction. The reaction can not proceed without catalyst (Table 3, Entry 1). PR is hard to catalyze the condensation of *p*-chlorobenzaldehyde with methyl cyanoacetate (Entry 2). The yield of the reaction catalyzed by PR and TEPA with the same content as the TEPA-PR is only 56% (Entry 3). When the functionalized resin TEPA-PR was used as the catalyst, the yield of target product is 97%, suggesting that the TEPA groups in the resin catalyst have high catalytic activity (Entry 7). Compared with various solvents (Entries 4～7), the TEPA-PR shows relatively better catalytic activity in polar protic solvents (Entries 6, 7), and the best catalytic activity was achieved in water (Entry 7). The result can be explained that polar protic solvents are conducive to the stability of transition state intermediates. Various of dosages of methyl cyanoacetate were investigated and the optimal dosage is 1.5 equiv. (Entries 7, 8). Additionally, different reaction times were detected and the best time is 5 h (Entries 7, 9～12). Different dosages of catalyst were tested and the best catalyst loading is 2.5 mol% (Entries 6, 16～18). Although the activity of the TEPA-PR is slightly lower than pyridinium acetate, it still has high activity (Entry 15). Furthermore, the Knoevenagel condensation reaction can be smoothly catalyzed by the TEPA-PR within 7 h at room temperature (Entries 11). Moreover, the reaction catalyzed by the TEPA-PR with different functionalities can get satisfactory yields, and the resin catalysts with large functionality are conducive to the catalysis of the reaction (Entries 7, 13, 14).

In summary, the reaction could reach the highest yield under the conditions of 2.5 mol% catalyst loading, 1.5 equiv. of methyl cyanoacetate, green solvent, 30 ℃ and 5 h (Entry 7).

2.2.2 Knoevenagel condensation reaction catalyzed by TEPA-PR

Various aromatic aldehydes and methyl cyanoacetate/malononitrile as substrates were used to detect the substrate applicability of the resin catalyst TEPA-PR for Knoevenagel condensation reaction. As shown in Table 4, the TEPA-PR can efficiently catalyze various target products with satisfactory isolated yields (81%～99%). In addition, the reactive activities of aromatic aldehydes with electron-withdrawing or electron-donating groups are higher than that of benzaldehyde (**1a**～**1g**). Although the reactive activity of ethyl cyanoacetate is lower than methyl cyanoacetate, the reaction can still be carried out at higher temperatures (**1k**～**1o**). The *p*-hydroxybenzaldehyde has high reactivity, which can be explained that the substrate can be easily enriched on the surface of resin through hydrogen bonding (**1f**). Furthermore, the activity of cinnamic aldehyde is higher than benzaldehyde because larger conjugate structure in the target product promote the formation of the

Table 3 Catalytic activities of the TEPA-PR for the Knoevenagel condensation reaction[a]

Entry	Solvent	Catalyst loading/mol%	Dosage of methyl cyanoacetate/equiv.	Temp./℃	Time/h	Yield[b]/%
1	H_2O	—	1.5	30	5	N.R.
2[c]	H_2O	0.1 g	1.5	30	15	44
3[d]	H_2O	2.5	1.5	30	5	56
4	Cyclohexane	2.5	1.5	30	5	41
5	CH_3CN	2.5	1.5	30	5	75
6	EtOH	2.5	1.5	30	5	80
7	H_2O	2.5	1.5	30	5	97
8	H_2O	2.5	1.2	30	5	92
9	H_2O	2.5	1.5	30	1	80
10	H_2O	2.5	1.5	30	3	87
11	H_2O	2.5	1.5	30	4	96
12	H_2O	2.5	1.5	25	7	97
13[e]	H_2O	2.5	1.5	30	5	96
14[f]	H_2O	2.5	1.5	30	5	84
15[g]	H_2O	2.5	1.5	30	1	97
16	H_2O	1	1.5	30	5	44
17	H_2O	5	1.5	30	5	96
18	H_2O	10	1.5	30	5	95

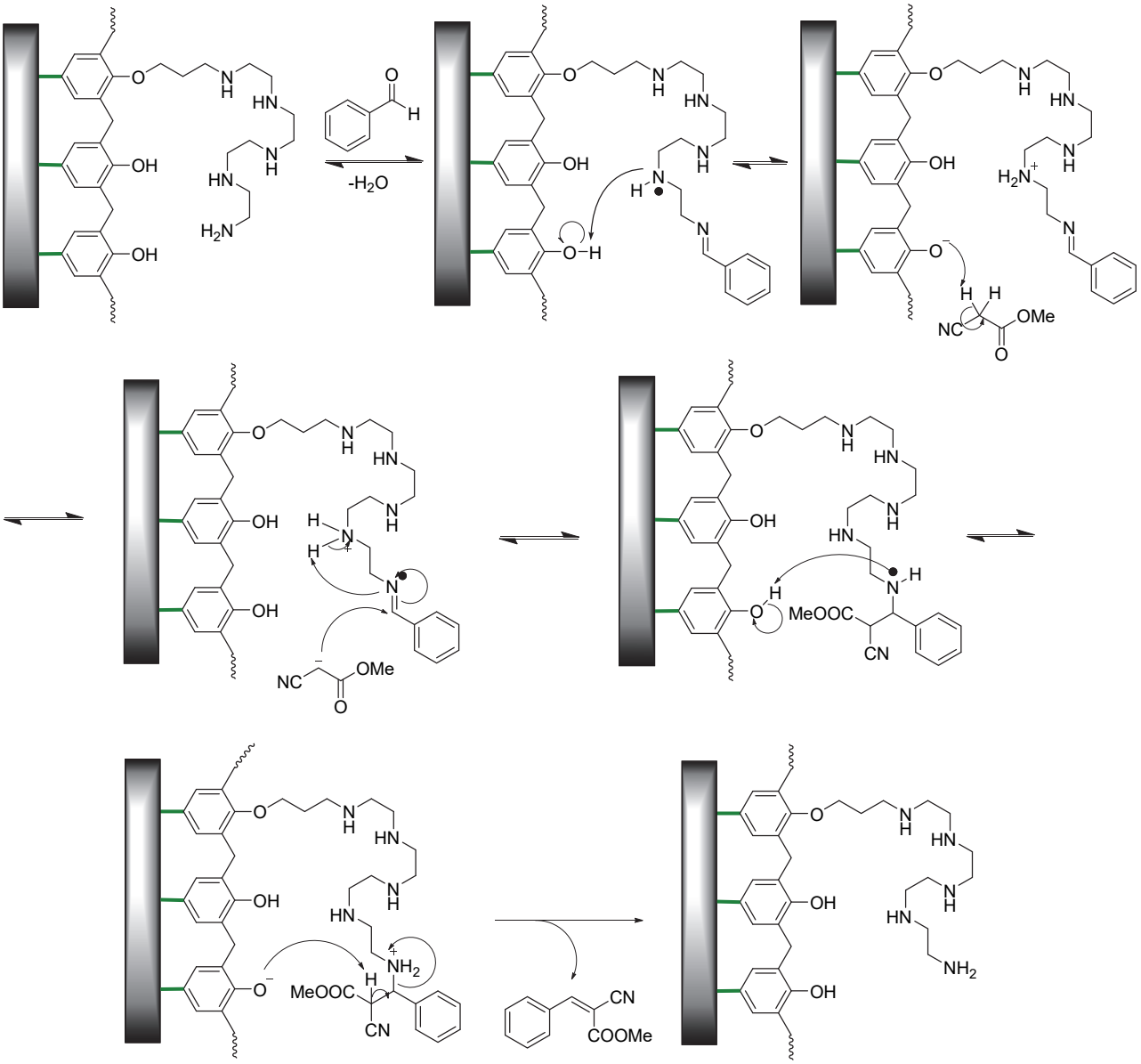
[a] General conditions: 1～10 mol% TEPA-PR, 1 mmol of aromatic aldehydes, 1.5 equiv. of methyl cyanoacetate, 10 mL of various solvents, and the reaction was carried out in a single neck flask at 30 ℃ for 1～5 h; [b] isolated yield; [c] 0.1 g of PR was used as catalyst; [d] The catalyst is TEPA and PR. The usage of TEPA is 4.7 mg, and the usage of PR is 20.9 mg; [e] The catalyst is TEPA-PR-1; [f] The catalyst is TEPA-PR-2; [g] The catalyst is pyridinium acetate.

products. Moreover, the reaction activity of malononitrile is higher than that of methyl cyanoacetate, and the reaction was completed within 30 min (**1i**, **1j**). The Knoevenagel condensation reaction of aliphatic aldehydes is difficult to be catalyzed by the TEPA-PR, and the substrates with weak electron-attracting methylene groups have low activity (see Supporting Information, Scheme S1). Therefore, the catalyst TEPA-PR has many highlights such as water phase catalysis, low catalyst loading (2.5 mol%), short reaction time (30 min～10 h) and high yields.

2.3 Reaction mechanism of Knoevenagel condensation reaction catalyzed by the TEPA-PR

The possible acid-base mechanism for the Knoevenagel condensation is shown in Scheme 2. Firstly, the benzaldehyde and primary amine form the imine species and release H_2O molecules. Then, the secondary amine species grabs the protons of the phenolic hydroxyl groups and forms protonated amine species. Secondly, the phenoxy anions capture a proton from ethyl cyanoacetate. Then, the activated C═N bond is attacked by the anion of ethyl cyanoacetate to form the corresponding adduct. Thirdly, the secondary amine species grab the protons of the phenolic hydroxyl groups and produce protonated imine species. Active protons in ethyl cyanoacetate are then attacked by phenol oxygen anions. Finally, the products are released, and the catalytic process is completed.

Additionally, the reaction mechanism is not unique, and other possible mechanism is shown in Scheme S2 ((see Supporting Information).



Scheme 2 Possible acid-base mechanism of Knoevenagel condensation reaction catalyzed by the TEPA-PR

2.4 Reusability and gram-scale experiments

Reusability is a main factor in evaluating the performance of heterogeneous catalysts. The Knoevenagel condensation reaction of *p*-chlorobenzaldehyde and malononitrile was chosen as a model reaction to detect the reusability of the catalyst TEPA-PR. As shown in Figure 4, after the TEPA-PR was used five or eight times, the yield of product can achieve 91% or 80%, demonstrating that the resin catalyst has good recyclability.

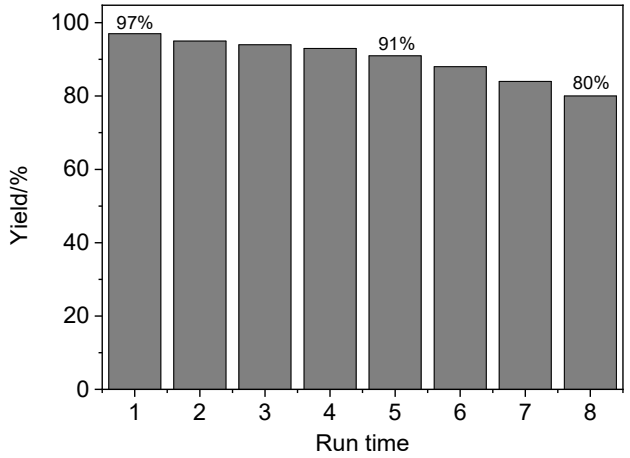
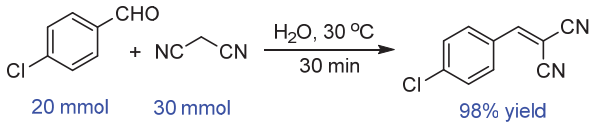


Figure 4 Reusability experiment of the TEPA-PR

The gram-scale experiment is important for evaluating the industrial application of the catalyst. The dosage of reactants was expanded to 20 times, and the isolated yield was as high as 98%, which shows that the resin catalyst TEPA-PR has good application potential in practical industrial production (Scheme 3).



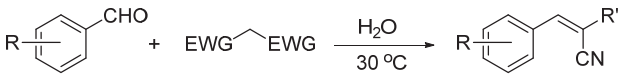
Reagents and conditions: 2.5 mol% TEPA-PR, 20 mmol of *p*-chlorobenzaldehyde, 30 mmol of malononitrile, 100 mL of H_2O, and in a single neck flask at 30 ℃ for 30 min

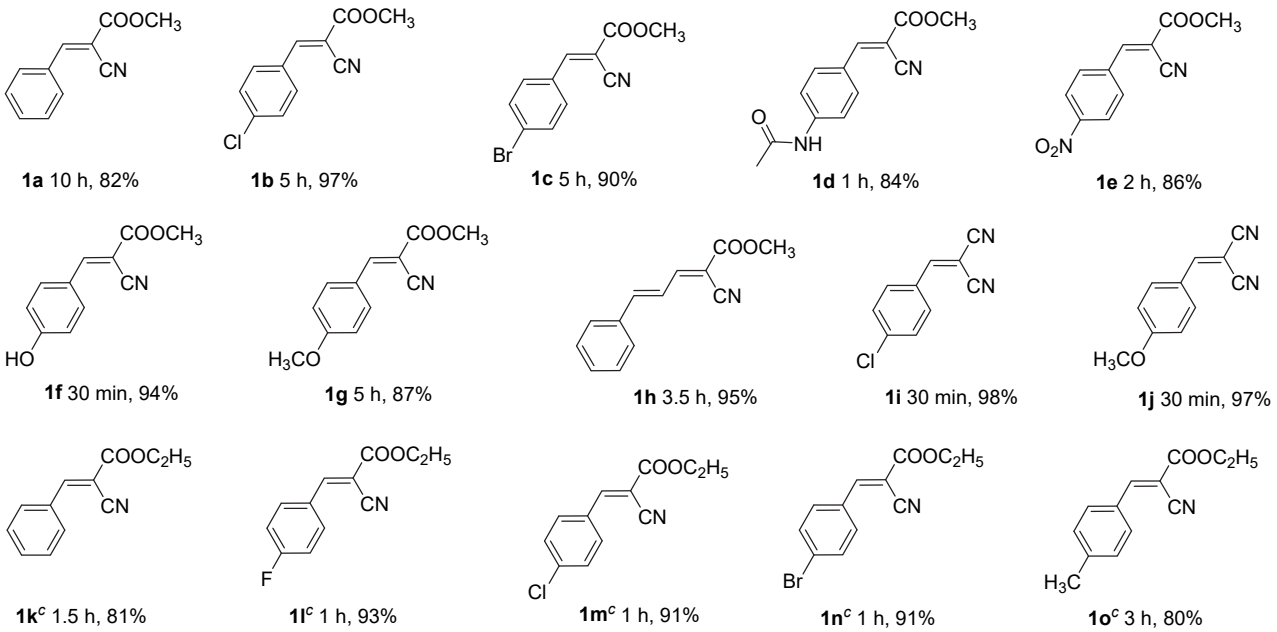
Scheme 3 Gram-scale experiment of the reaction catalyzed by the TEPA-PR

2.5 Comparison of the TEPA-PR with other catalytic systems

Compared with other catalysts for Knoevenagel condensation reaction of *p*-chlorobenzaldehyde and malononitrile, the resin-supported TEPA catalyst exhibits excellent performance (Table 5). Although some catalytic systems have low temperature, they can not conduct within short time and get satisfactory reusability (Table 5, Entries 2, 6, 7). Noteworthily, the Knoevenagel condensation reaction catalyzed by the TEPA-PR has the advantages of water phase catalysis, mild conditions, high yield and good cycle performance.

Table 4 TEPA-PR-catalyzed Knoevenagel condensation reaction of various substrates[a,b]





[a] General conditions: 2.5 mol% TEPA-PR, 1 mmol of aromatic aldehydes, 1.5 equiv. of methyl cyanoacetate/malononitrile/ethyl cyanoacetate, 10 mL of H_2O, and the reaction was carried out in a single neck flask at 30 ℃ for 30 min～10 h; [b] isolated yield. [c] The reaction temperature is 80 ℃

Table 5 Comparation of different catalytic system of catalyzing Knoevenagel condensation reaction

Entry	Cat./cat. amount	Solvent	T/℃	Time/min	Yield/%	Run[b]	Ref.
1	Co(II)-organic frameworks/2 mol%	MeOH	25～30	60	96	—	[12]
2	Sulfunic acid functionalized polymer (PHSA)/30 mg	H_2O	r.t.	180	100	5	[13]
3	V-Zn-MOF/2 mol%	None	60	180	99	10	[14]
4	DABCO-based bis-dicationic ionic salt catalyst/30 mg	H_2O	85	8	95	3	[15]
5	Mg-Si-ZSM-12/100 mg	EtOH	70	240	100	5	[16]
6	$K_7HNb_6O_{19}$•$13H_2O$/20 mg	EtOH	r.t.	45	100	3	[17]
7	MOF-NH2/13 mol%	DMF	80	240	97	5	[18]
8	Microporous organic polymer Fe-POP-1/	$V(H_2O)$∶V(EtOH)=1∶1	r.t.	300	96	—	[19]
9	Three pyrazole-3-carboxylic acid complexes/6 mol%	None	50	300	93	3	[20]
10	TEPA-PR/2.5 mol% (25 mg)	H_2O	30	30	98	5	This work

[a] Reaction conditions: 4-boromobenzaldehyde (1 mmol), 2- aminobenzamide (1 mmol) and ethanol solvent (10 mL) under reflux conditions; [b] Run times with the yield higher than 90%.

3 Conclusions

The acid-base bifunctional catalyst TEPA-PR has been successfully prepared for the first time. Through exploring reaction conditions, we found that the resin-catalyzed reaction system has many advantages, such as water phase catalysis, efficient catalytic activity and mild reaction conditions. Furthermore, the TEPA-PR can efficiently catalyze Knoevenagel condensation reaction with broad substrate applicability, getting satisfactory isolated yields of 80%～99%. Moreover, the TEPA-PR can be used 5 times without significant in catalytic activity, and it exhibits good catalytic activity in the gram-up experiment, suggesting that the TEPA-PR has application value in the industrial production.

4 Experimental section

4.1 Reagents

Commercially available phenolic resin was stored in a desiccator at 60 ℃ before use. The chemicals of tetraethylenepentamine, aromatic aldehydes, methyl cyanoacetate, malononitrile, 1,3-dibromopropane, organic solvents and K_2CO_3 were purchased commercially. Moreover, water is deionized.

4.2 Instruments

The fourier transform infrared spectra (FT-IR) of PR, Br-PR and TEPA-PR were tested by the AVATAR360 FTIR spectrometer (Thermo Nicolet). The C, H and N contents of the Br-PR and the TEPA-PR were determined by an Elementar Vario MACRO cube (Germany). The XRD spectra of original and functionalized resins were detected by a D/MAX-2500 X-ray diffractometer (Rigaku Corporation). The X-ray photoelectron spectra (XPS) of the TEPA-PR were measured by a PH1600 spectrometer (PERKIN ELMER).

4.3 Preparation of functionalized resins

Preparation of the Br-PR: 10.2 g of PR, 13.8 g of K_2CO_3, 20.2 g of 1,3-dibromopropane and 100 g of CH_3CN were added to a single-necked flask and refluxed for 12 h. Then, the functionalized resin was taken out, washed with 200 mL of water, and then dried at 60 ℃ over night. The weight gain of resin is 17.3%.

Preparation of the TEPA-PR: 3.64 g of Br-PR, 35 mL of tetraethylenepentamine and 45 mL of ethanol were added to a single-necked flask and refluxed for 24 h. Then, the resulting TEPA-PR was taken out and cleaned with 100 mL of ethanol, and then the TEPA-PR was dried overnight at 60 ℃.

4.4 General procedure for the Knoevenagel condensation reaction

Aromatic aldehydes (1 mmol), methyl cyanoacetate or malononitrile (1.2～1.5 mmol) and 2～10 mol% TEPA-PR were added to a glass stopper tube. The reaction was reacted at 30～50 ℃ for appropriate time. After the reaction was finished, the TEPA-PR was filtered out and washed with ethyl acetate (5 mL), the aqueous phase was extracted with ethyl acetate (10 mL×3), and the organic phase was combined. The combined organic solution was concentrated and the crude reaction product was purified by column chromatography (petroleum ether/ethyl acetate, V∶V=10∶1～1∶1).

Methyl (*E*)-2-cyano-3-phenyl-2-propenoate (**1a**): 0.1535 g, 82% yield. m.p. 87～89 ℃ (lit.[21] 87.9 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27 (s, 1H), 8.00 (d, J=7.7 Hz, 2H), 7.60～7.54 (m, 1H), 7.51 (t, J=7.5 Hz, 2H), 3.94 (s, 3H).

Methyl (*E*)-2-cyano-3-(4-chlorophenyl)-2-propenoate (**1b**): 0.2145 g, 97% yield. m.p. 121～123 ℃ (lit.[22] 122 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (s, 1H), 7.94 (d, J=8.5 Hz, 2H), 7.49 (d, J=8.6 Hz, 2H), 3.95 (s, 3H).

Methyl (*E*)-2-cyano-3-(4-bromophenyl)-2-propenoate (**1c**):[23] 0.2401 g, 90% yield. m.p. 99～100 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (s, 1H), 7.86 (d, J=8.5 Hz, 2H), 7.65 (d, J=8.5 Hz, 2H), 3.94 (s, 3H).

Methyl 3-(4-(acetylamino)phenyl)-2-cyano-2-propenoate (**1d**):[24] 0.2048 g, 84% yield. m.p. 241～242 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.45 (s, 1H), 8.29 (s, 1H), 8.04 (s, 2H), 7.79 (s, 2H), 3.85 (s, 3H), 2.11 (s, 3H).

Methyl (*E*)-2-cyano-3-(4-nitrophenyl)-2-propenoate

(**1e**): 0.2002 g, 86% yield. m.p. 170～172 ℃ (lit.[25] 172～173 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27 (s, 1H), 8.07 (d, J=8.3 Hz, 2H), 7.80 (d, J=8.4 Hz, 2H), 3.97 (s, 3H).

Methyl (*E*)-2-cyano-3-(4-hydroxyphenyl)-2-propenoate (**1f**): 0.1916 g, 94% yield. m.p. 212～214 ℃ (lit.[26] 211℃); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.84 (s, 1H), 8.25 (s, 1H), 8.01 (d, J=8.7 Hz, 2H), 6.96 (d, J=8.7 Hz, 2H), 3.83 (s, 3H).

Methyl (*E*)-2-cyano-3-(4-methoxyphenyl)-2-propenoate: (**1g**): 0.1883 g, 87% yield. m.p. 104～106 ℃ (lit.[21] 104.1 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (s, 1H), 8.01 (d, J=8.8 Hz, 2H), 7.00 (d, J=8.8 Hz, 2H), 3.91 (d, J=4.2 Hz, 3H), 3.90 (s, 3H).

Methyl (2*E*,4*E*)-2-cyano-5-phenyl-2,4-pentadienoate (**1h**):[26] 0.2021 g, 95% yield. m.p. 141～143 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08～7.95 (m, 1H), 7.59 (dd, J=6.5, 2.9 Hz, 2H), 7.46～7.35 (m, 3H), 7.33～7.23 (m, 2H), 3.86 (m, 3H).

2-((4-Chlorophenyl)methylene)-propanedinitrile (**1i**): 0.1506 g, 98% yield. m.p. 161～163 ℃ (lit.[27] 161～162 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J=8.6 Hz, 2H), 7.74 (s, 1H), 7.52 (d, J=8.6 Hz, 2H).

2-((4-Methoxyphenyl)methylene)-propanedinitrile (**1j**): 0.1784 g, 97% yield. m.p. 111～113 ℃ (lit.[25] 110～112 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, J=8.8 Hz, 2H), 7.65 (s, 1H), 7.26 (s, 1H), 7.02 (d, J=8.9 Hz, 2H), 3.92 (s, 3H).

Ethyl (*E*)-2-cyano-3-phenyl-2-propenoate (**1k**): 0.1626 g, 81% yield. m.p. 46～48 ℃ (lit.[25] 47～49 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (s, 1H), 8.06～7.88 (m, 2H), 7.62～7.44 (m, 3H), 4.39 (q, J=7.1 Hz, 2H), 1.41 (t, J=7.1 Hz, 3H).

Ethyl (*E*)-2-cyano-3-(4-fluorophenyl)-2-propenoate (**1l**): 0.2029 g, 93% yield. m.p. 94～95 ℃ (lit.[25] 94～96 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (s, 1H), 8.10～7.93 (m, 2H), 7.24～7.14 (m, 2H), 4.39 (q, J=7.1 Hz, 2H), 1.41 (t, J=7.1 Hz, 3H).

Ethyl (*E*)-2-cyano-3-(4-chlorophenyl)-2-propenoate (**1m**): 0.2145 g, 91% yield. m.p. 164～166 ℃ (lit.[25] 163～165 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (dd, J=8.4, 2.1 Hz, 1H), 7.72～7.59 (m, 1H), 7.50 (t, J=1.7 Hz, 1H), 6.23 (d, J=1.5 Hz, 1H), 6.01 (s, 1H), 3.95 (d, J=1.9 Hz, 3H).

Ethyl (*E*)-2-cyano-3-(4-bromophenyl)-2-propenoate (**1n**):[28] 0.2528 g, 91% yield. m.p. 129～131 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (s, 1H), 7.86 (d, J=8.4 Hz, 2H), 7.65 (d, J=8.4 Hz, 2H), 4.39 (q, J=7.1 Hz, 2H), 1.40 (t, J=7.1 Hz, 3H).

Ethyl (*E*)-2-cyano-3-(4-methylphenyl)-2-propenoate (**1o**): 0.1844 g, 80% yield. m.p. 91～92 ℃ (lit.[29] 163～165 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (s, 1H), 7.90 (d, J=7.9 Hz, 2H), 7.42～7.20 (m, 2H), 4.44～4.26 (m, 2H), 2.43 (s, 3H), 1.40 (t, J=7.1 Hz, 3H).

Supporting Information ^{1}H NMR spectra of products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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(Fan, Y.)

