

Overcoming acid–base copolymer neutralization using mesoporous carbon and its catalytic activity in the tandem deacetalization–Knoevenagel condensation reaction

Roozbeh Javad Kalbasi¹ · Fatemeh Rahmati² · Omid Mazaheri^{3,4}

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Abstract

Acid–base copolymer materials are of considerable interest because of their fundamental implications for acid–base bifunctional catalysis applications. However, quenching the acid and base sites of the copolymer with each other in free radical polymerizations is still challenging. Herein, we demonstrate that the polymerization of styrenesulfonic acid-co-4-vinylpyridine into the mesoporous carbon material (i.e., CMK-3) can control the chain growth polymerization and result in decreasing the interaction of the acid–base sites. The results showed that by using CMK-3, 40% of the acid and base sites of the copolymer remain in their original form while 60% of acid and base sites convert to the pyridinium and sulfonate forms. Furthermore, it is demonstrated that this material can be processed as a heterogeneous bifunctional acid–base catalyst in the tandem one-pot acid–base reaction (i.e., deacetalization– Knoevenagel condensation reaction) with a high catalytic activity in aqueous media.

Fatemeh Rahmati rahmaty_f@yahoo.com

Omid Mazaheri mazaherio@unimelb.edu.au

- ¹ Faculty of Chemistry, Kharazmi University, Tehran, Iran
- ² Department of Chemistry, Shahreza Branch, Islamic Azad University, Isfahan 311-86145, Iran
- ³ School of Agriculture and Food, Faculty of Veterinary and Agricultural Sciences, The University of Melbourne, Parkville, VIC 3010, Australia
- ⁴ Department of Chemical Engineering, The University of Melbourne, Parkville, VIC 3010, Australia

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Roozbeh Javad Kalbasi rkalbasi@khu.ac.ir; rkalbasi@gmail.com

Graphic abstract



Keywords Acid–base copolymer \cdot Mesoporous carbon CMK-3 \cdot Acid–base neutralization sites \cdot Styrenesulfonic acid \cdot 4-vinylpyridine \cdot Tandem deacetalization–Knoevenagel condensation

Introduction

Nowadays, tandem organic reactions are getting attractions in modern chemical industries due to decreasing the time process and reducing the waste generated [1-7]. Typically, the presence of acid–base sites in catalysts, which are known as bifunctional catalysts, is required to fulfill the tandem organic reactions [8–11]. However, the neutralization and deactivation of the acid and base sites of the polymer when the acid and base sites are adjacent to each other are still challenging [12–15].

Over the last two decades, several acid–base catalysts in which basic groups are amines, pyridine, and imidazole and acidic groups are sulfonic acids, acrylic acids, and carboxylic acids were synthesized [8, 16–18]. One method to create the acid–base sites in materials is using the acid- and base-functionalized polymers [19–22]. The procedure is included in blending two synthesized polymers (acid and base polymer, separately) [23]. Here, cationic ($-SO_3H$) and anionic ($-CH_2NH_2$) polymers are usually mixed to induce acidic and basic properties. Although this procedure is simple, as the acid and base polymers are blending, the acid and base active sites have high interactions with each other, and as a corollary of this, the catalyst is neutralized [21, 24]. To overcome with neutralization of acid and base sites, benzene as a spacer is used in the copolymer structure [25–27]. However, the time-consuming procedure, its toxicity, and difficulty decline the privilege.

Besides, post-grafted and bridging are common methods to utilize organosilanes (containing -SH and SO₂Cl functional groups) on the support materials (usually porous structure materials) [28–32]. Here, the functional groups of the organosilanes are oxidized to convert to the acidic groups ($-SO_3H$). Multi-step procedure to graft the organosilanes and the high cost of the organosilanes reduce the attention to use these methods. Moreover, the unprotected acid and base groups in the organosilanes may be quenched [33]. Another method to decrease the acid–base quenching is co-condensation [12]. Nevertheless, a substantial obstacle in this method is an incapacity to completely take away the template by neither solvent nor rising temperature methods. Thus, measuring the content of organic materials by the thermogravimetric analysis in the support material is demanding.

Using porous carbon materials such as nanotubes, CMK-n, and 3DOMs (3D ordered macroporous) and MOFs (Metal–Organic Frameworks) as the polymer support has some advantages thanks to having high surface area and good connection between polymer and carbon porous material [10, 34–38]. By this method, the base and acid polymers become farther from each other, which leads to a decrease in the neutralization [39]. As the mesoporous carbons have a high surface area and several interconnected pores, the polymers can disperse throughout the pores. Thus, the porous carbon can prevent the acid and base sites of the copolymer from neutralization [35].

In our previous works, synthesis of acid or base polymers in porous materials (i.e., mesoporous silica and carbon) by utilizing simultaneous method was described [40, 41]. In this method, the monomer cannot grow thoroughly into the pores which led to the homopolymer formation (not a bulk polymer).

In this study, we prompt to synthesize acid–based copolymer (poly(styrenesulfonic acid-co-4-vinylpyridine)) (poly(SSA-co-4VP)) with the simultaneous method without using spacers, protecting compounds, or organosilanes functionalization (i.e., post-grafted, bridging, and co-condensation) into the mesoporous carbon CMK-3. To the best of our knowledge, trapping acid–base copolymer into the mesoporous carbon has rarely been applied to overcome the neutralization of acid–base sites polymer. After the synthesis of materials, we utilize the material as a catalyst in the deacetalization–Knoevenagel condensation reaction.

Results and discussion

Catalyst characterization

X-ray powder diffraction (XRD)

Figure 1 shows significant diffraction peaks at around $2\theta = 1^{\circ}-2^{\circ}$ in the XRD patterns of CMK-3 and poly(SSA-co-4VP)/CMK-3. The peaks are attributed to (100) reflection of 2D ordered 2D hexagonal structure [42–44]. The diffraction peak of poly(SSA-co-4VP)/CMK-3 has been shifted to 1.3° from 1.15°, which can be explained by incorporation of the copolymer into the mesoporous carbon CMK-3 and slight decrease in its pore size [45]. Moreover, the intensity of the main peak



Fig. 1 XRD patterns of CMK-3 and poly(SSA-co-4VP)/CMK-3

in the poly(SSA-co-4VP)/CMK-3 reduces demonstrating the existence of the copolymer into the mesopores of CMK-3. It also can be related to the dilution of the CMK-3 by the copolymer. However, the survival of diffraction peak at $2\theta = 1.3^{\circ}$ shows that the CMK-3 structure is retained.

FT-IR analysis

The FT-IR spectra of CMK-3 and poly(SSA-co-4VP)/CMK-3 are represented in Fig. 2. No tangible absorption is detected in CMK-3 indicating the formation of graphitic frameworks during the carbonization of sucrose [46]. On the other hand, some



Fig. 2 FT-IR spectra of CMK-3 and poly(SSA-co-4VP)/CMK-3

new peaks have appeared in the poly(SSA-co-4VP)/CMK-3, which is attributed to the presence of the polymer. In detail, the peaks at 2857, 2933, and 3046 cm⁻¹ are related to the aliphatic and aromatic stretching vibration of C–H bonds [45]. The broad absorption peak of –OH stretching vibration is observed between 3100 and 3700 cm⁻¹, which is related to either adsorption of water by the polymer and mesoporous carbon CMK-3 and/or –OH groups of PVSA (polyvinyl sulfonic acid) [47, 48]. Two stretching vibration peaks at 1568 and 1415 cm⁻¹ can be assigned to the pyridine rings [25, 49]. Moreover, the pyridinium cation absorption at 1638 cm⁻¹ is related to the zwitterion state formation [25]. Two sharp peaks at 1185 and 1209 cm⁻¹ are attributed to the S=O groups of the polymer that arises from the asymmetric stretching vibration [25, 27]. The stretching vibration of the S–O(H) in –SO₃H groups of the polymer shows an absorption band at 909 cm⁻¹ [25]. The other peaks at 1007, 1040, and 1124 cm⁻¹ can be attributed to both the aromatic rings and –SO₃H groups of the copolymer [50]. From these pieces of evidence, the formation of acid–base copolymer into the CMK-3 pores can be justified.

N₂ adsorption-desorption isotherm

The chemisorption and physisorption of CMK-3 and poly(SSA-co-4VP)/CMK-3 have been investigated and are shown in Fig. 3. As can be seen, both samples demonstrate adsorption isotherms of type IV with H₄ hysteresis loop and the capillary condensation between 0.3 and 0.8 relative pressure [44, 45, 51]. The BET surface area of CMK-3 and poly(SSA-co-4VP)/CMK-3 is 1527 and 395 m² g⁻¹, respectively (Table 1). Moreover, the mesoporous volume of poly(SSA-co-4VP)/CMK-3 has been decreased by almost double (from 1.26 to 0.6 m³ g⁻¹) showing the incorporation of polymer into the porous carbon. The slight decrease in the pore size diameter has been observed when the polymers have been deposited into the mesopores CMK-3. All the BET surface area, mesoporous volume, and pore size diameter data



Fig. 3 N2 adsorption-desorption isotherms of CMK-3 and poly(SSA-co-4VP)/CMK-3

Sample	BET surface area $(m^2 g^{-1})$	$V_P (\mathrm{cm}^3 \mathrm{g}^{-1})^{\mathrm{a}}$	$D_p (\mathrm{nm})^{\mathrm{b}}$	$S_m (m^2 g^{-1})^c$
Mesoporous carbon CMK-3	1527	1.26	3.3	473
Poly(SSA-co-4VP)/CMK-3	395	0.6	3.1	295

Table 1 Physicochemical properties of the mesoporous carbon CMK-3 and poly(SSA-co-4VP)/CMK-3 samples obtained from $\rm N_2$ adsorption–desorption

^aTotal pore volume determined by the BET method

^bMesopore diameter determined by BJH method

^cThe micropore surface area was estimated by *MP*-plot

are shown that the copolymer is incorporated into the CMK-3. According to the MP plot data, both samples portray microstructure (473 and 295 m² g⁻¹ for CMK-3 and poly(SSA-co-4VP)/CMK-3, respectively) (Table 1) representing that after the polymerization of monomers, the microchannels have not been blocked. The existence of microchannels facilitates the transformation of substrates in the catalytic application by decreasing the mesoporous blocking.

Thermal property

Figure 4 presents the TGA curve of poly(SSA-co-4VP)/CMK-3 under N₂ atmosphere. The poly(SSA-co-4VP)/CMK-3 thermograph depicts two mass loss steps. The first step occurs behind 160 °C which is corresponded to the desorption of water from both support (CMK-3) and copolymer with around 7.5% w/w mass loss. The material is losing mass around 22.5% w/w between 170 and 700 °C which is related to the decomposition of the copolymer. With a comparison between the weight loss of copolymer trapped into the mesoporous CMK-3 and the conventional copolymer [24], the traditional poly(SSA-co-4VP) has a major weight loss around 92%, which begins at 350 °C and ends at 430 °C [24]. Demonstrably, the poly(SSA-co-4VP)/CMK-3 nanocomposite displays a slower degradation rate than traditional poly(SSA-co-4VP) which is related to the higher thermal stability of the composite. It can be authorized by anchoring the copolymers into the mesopores of CMK-3.

Morphology study (SEM and TEM)

The surface morphology of mesoporous carbon CMK-3 and poly(SSA-co-4VP)/ CMK-3 has been investigated using SEM (Fig. 5a, b). As can be seen, the shape and morphology of poly(SSA-co-4VP)/CMK-3 are similar to the CMK-3 with a worm-like structure [52, 53]. No significant change is observed in the SEM image in the second sample (poly(SSA-co-4VP)/CMK-3) (Fig. 5b). It may show that the polymerization of vinyl sulfonic acid and vinyl pyridine mainly occurred into the CMK-3 pores. It is correspondent with the lower pore volume, smaller pore diameter, and lower surface area of poly(SSA-co-4VP)/CMK-3 in the BET results. Thus, the CMK-3 structure can provide appropriate support for lying the copolymer due to having a large amount of volume and surface area.



Fig. 4 TGA curves of poly(SSA-co-4VP)/CMK-3



Fig.5 SEM images of CMK-3 (a) and poly(SSA-co-4VP)/CMK-3 (b), TEM images of CMK-3 (c) and poly(SSA-co-4VP)/CMK-3 (d)

The TEM images of poly(SSA-co-4VP)/CMK-3 are illustrated in Fig. 5c, d. The mesostructured CMK-3 is observed in both CMK-3 and poly(SSA-co-4VP)/CMK-3 samples which indicates that after the polymerization, the CMK-3 structure is retained [52]. However, the presence of copolymer into the mesoporous is not detected because of almost identical carbon-based composite materials of CMK-3 with polymers using the TEM technique.

Potentiometric titration

To evaluate the neutralization of copolymer, the acid and base sites of poly(SSAco-4VP)/CMK-3 have been estimated by potentiometric titration. For measuring acid sites, two equivalence points by consuming NaOH have been observed in 1.9 and 5.7 mL. According to the experiment content of styrene sulfonic acid and 4-vinylpyridine monomers in the catalyst (10 mg SSA and 10 mg 4-VP in 50 mg of the catalyst), 4 mg sulfonic acid and 6 mg pyridinium ion have been formed in the material. Besides, to measure basic sites, HCl has been used for detecting the first and second equivalence points. The total amount of sulfonated form and pyridine forms was 6 mg and 4 mg, respectively.

Consequently, almost 40% of copolymer sites remained in their acid and base forms and 60% are in the pyridinium and sulfonate forms. Remaining 40% acid and base forms without using a complex technique (i.e., spacer or co-condensation) is noteworthy as in the most literature, zwitterion form of the acid–base copolymer has been formed and a few amount of acid and base sites remained even by using spacer method [25, 27, 54]. Therefore, the CMK-3 mesoporous structure can act as a spacer in the material and no further chemical spacer (i.e., benzene) acquires to separate the acid and base sites. It demonstrates that this method is effective to separate the acid and base sites in the copolymer.

Catalytic activity

Reaction optimization

The synthesized poly(SSA-co-4VP)/CMK-3 is utilized as a bifunctional catalyst in the deacetalization–Knoevenagel condensation reaction. At first, the activity of catalyst has been maximized by optimization of acid and base monomers' molar ratios, the content of CMK-3 and the catalyst, solvent types, and temperatures, which is tabulated in Table 2. Then, the catalytic activity has been investigated using some dimethyl acetal with ethyl cyanoacetate substitutes. Finally, the reusability and the heterogeneity of the catalyst have been evaluated.

The optimization of the SSA/4-VP molar ratio can promote the activity of the catalyst in both steps of the reaction (deacetalization and Knoevenagel steps); by decreasing the molar ratio of SSA/4-VP from 3:2 to 1:2, the catalytic activity increases. Indeed, by increasing the number of acid sites (SSA), the tendency of neutralization with base sites increases (entries 1–3). By changing the content of CMK-3 in poly(SSA-co-4VP)/CMK-3 from 0.125 to 0.5 g, the reaction time

Table 2 Measurement of aci-	d and base sites and z	zwitterion in the cat	talyst via potention	netric titration					
Potentiometric titration	Poly(SSA-co- 4VP)/CMK-3 (mg)	V _{1-NaOH} (mL) ^a	V _{2-NaOH} (mL) ^b	V _{1-HCl} (mL) ^c	V _{2-HCl} (mL) ^d	$W_1 (\mathrm{mg})^{\mathrm{e}}$	W ₂ (mg) ^f	$M_1 (\mathrm{mg})^{\mathrm{g}}$	$M_2 (\mathrm{mg})^{\mathrm{g}}$
Measurement of acid sites	50	1.9	5.7	1	I	10	10	4^{h}	6
Measurement of basic sites	50	I	I	3.0	3.9	10	10	6 ⁱ	$4^{\rm k}$
^a The amount of consumed N	aOH according to the	e first equivalence p	ooint						
^b The amount of consumed N	aOH according to the	e second equivalent	ce point						
^c The amount of consumed H	Cl according to the fi	îrst equivalence poi	int						
^d The amount of consumed H	Cl according to the s	second equivalence	point						
^e The amount of styrene sulfo	mic acid in the cataly	/st							
^f The amount of 4-vinyl pyrio	line in the catalyst								
^g The amount of acid and bas	e sites measurement	by potentiometric ti	itration						
^h The amount of styrene sulfo	nic acid								
ⁱ The amount of styrene sulfo	nate								
^j The amount of protonated 4.	-vinyl pyridine								
^k The amount of 4-vinylpyrid	ine								

decreases from 210 to 75 min, and subsequently, the product yield increases up to 92% (entries 3–6). From the spatial aspects, the copolymer chains trap in a small confide space and it prevents the entanglement in the mesopores of CMK-3; thus, the acid–base sites of the copolymer are protected from neutralization (Scheme 1) [36]. Another reason to increase the catalytic activity in the poly(SSA-co-4VP)/CMK-3 is that the mesoporous carbon CMK-3 provides a high surface area in the catalyst and it can increase the speed and yield of the reaction by increasing the chance of interaction between the reactants and the acid–base sites [31, 55, 56].

By raising the temperature from 40 to 60 °C, the reaction time and yield improve to 75 min and 87%, respectively; however, no tangible improvement is detected by increasing the temperature to 90 °C (entries 3, 7, 8). The amount of catalyst also has been optimized in which the reaction time and yield remain constant above 0.1 g of the catalysis uses (entries 8–11). Accordingly, 0.1 g catalyst with the 1:2 SSA/4-VP molar ratio at 60 °C in water as a solvent has been elected as the optimized conditions.

The tandem reactions without the poly(SSA-co-4VP)/CMK-3 and using only the acidic and/or basic polymer in the solvent-free condition have been surveyed (entries 12–14). The reaction cannot progress in the absence of the acid sites. However, by using the acid polymer (SSA) in the tandem reaction, almost all benzaldehyde dimethyl acetal is converted to benzaldehyde. It demonstrates that the reaction needs both acidic and basic components [57, 58]. Since water is well known as a green solvent and the reaction has been advanced in an appropriate time, no further investigation on other solvents has been fulfilled. However, the solvent-free condition has been examined, which produced a lower product yield in higher reaction time (entry 15).

The reaction with the electron-withdrawing group $(-Cl, -Br \text{ and } -NO_2)$ and the electron-donating group $(-OCH_3)$ substitutes has been studied in the optimized catalyst conditions and is tabulated in Table 3. As can be seen, the reaction time reduces when the electron-withdrawing groups are on the benzaldehyde dimethyl acetal while the slight change is observed in the presence of the electron-donating



Scheme 1 Schematic of SSA-co-4VP polymerization into the mesoporous carbon CMK-3 and its catalytic activity in the tandem deacetalization–Knoevenagel condensation reaction

Entry	SSA (mmol) ^a	4-VP (mmol) ^a	SSA/4-VP ratio	CMK-3 (g)	Catalyst (g)	<i>T</i> (°C)	Time (min)	Yield (%) ^b
1	0.032	0.018	3:2	0.5	0.1	90	420	70
2	0.024	0.027	1.5:2	0.5	0.1	90	300	72
3	0.019	0.039	1:2	0.5	0.1	90	75	92
4	0.019	0.039	1:2	0	0.01	90	280	55
5	0.019	0.039	1:2	0.12	0.1	90	210	70
6	0.019	0.039	1:2	0.25	0.1	90	180	75
7	0.019	0.039	1:2	0.5	0.1	40	75	47
8	0.019	0.039	1:2	0.5	0.1	60	75	87
9	0.019	0.039	1:2	0.5	0.06	60	420	45
10	0.019	0.039	1:2	0.5	0.08	60	360	70
11	0.019	0.039	1:2	0.5	0.12	60	75	87
12	0	0	-	0	0	60	200	0
13	0.019	0	-	0.5	0.1	60	50	0 (97) ^c
14 ^d	0	0.039	-	0.5	0.1	60	70	82
15 ^e	0.019	0.039	1:2	0.5	0.1	-	110	65

 Table 3
 Optimization of different factors on the catalytic activity of the poly(SSA-co-4VP)/CMK-3 in deacetalization–Knoevenagel condensation reaction

Reaction conditions: benzaldehyde dimethyl acetal (1.87 mmol), ethyl cyanoacetate (1.87 mmol), $\rm H_2O$ (4 mL)

^aBased on experimental adding

^bIsolated yield of benzylidene ethyl cyanoacetate

^cIsolated yield of benzaldehyde

^dReaction condition: benzaldehyde (1.87 mmol), ethyl cyanoacetate (1.87 mmol), H_2O (4 mL)

^eThe reaction has been accomplished in solvent-free conditions

group ($-OCH_3$ and -OH). Meanwhile, the yield of the products in all cases remained almost constant.

According to the mechanism pathway illustrated in Scheme 2, the reaction pathway contains two steps [58, 59]. During the first stage, the acid sites of the catalyst facilitate the deacetalization via formation of the carbocation and subsequently benzaldehyde production [60]. Then, the basic sites of the catalyst catalyze the reaction by taking the H- α of ethyl cyanoacetate as a methylene active compound to react with benzaldehyde. Regarding the electron-withdrawing groups, the possibility of the carbanion attack to the carbonyl group is more when compared to that of electron-donating groups [59]. Because the carbonyl group is more activated, the ethyl cyanoacetate can easily attack the carbonyl group of benzaldehyde [61].

The heterogeneity and reusability study

The catalyst heterogeneity has been checked by removing the catalyst from the middle of the reaction. For this purpose, after processing the reaction up to almost 50% in the Knoevenagel step, the catalyst has been removed while



Scheme 2 A plausible reaction mechanism for the deacetalization–Knoevenagel condensation reaction by poly(SSA-co-4VP)/CMK-3

the continuation of the reaction was being monitored. The result showed that no further C-C coupling reaction occurred, and the heterogeneous nature of the catalyst has been proved.

The activity of the reused catalyst has been checked based on the previous reports via simple filtration of the catalyst from the reaction and further washing with hot water and drying in vacuumed oven at 40 °C overnight [62]. It should be mentioned that the poly(SSA-co-4VP) has an adhesive feature and makes it hard to remove from the flask; on the other hand, the incorporation of the polymer into the mesoporous carbon CMK-3 led to having the powdery formation and facilitates to reuse and recover the catalyst. The outcomes authenticate that the catalyst can be recycled over 13 times with almost 10% lessening in the product yield. Moreover, only 7-10% polymer leaching has been detected by CHNS and potentiometric titration methods that introduces the heterogeneity nature of the catalyst. Besides, the SEM images of the recovered catalyst (after the sixth run of the reaction) are displayed in Fig. 6. In the XRD pattern of reused catalyst (Fig. 7), the main peak is shifted to higher 2 theta value, which can be explained by deformation of the polymer into the CMK-3 pores and subsequently blocking the mesopores [63]. However, comparing these images with the fresh catalyst (Fig. 5a, b), the CMK-3 mesostructure in the reused catalyst is well retained (Fig. 7).

The catalyzed activity of various catalysts in the deacetalization–Knoevenagel condensation reaction was compared with the synthesized catalyst in this study and is tabulated in Table 4. As can be seen, mostly the deacetalization–Knoevenagel condensation reactions process in organic solvents and/or high reaction time, which can be related to the lower catalytic activity of the catalysts.



Fig. 6 SEM images of the reused poly(SSA-co-4VP)/CMK-3 after the sixth run



Fig. 7 XRD pattern of the reused poly(SSA-co-4VP)/CMK-3 after the sixth run

Catalyst chemoselectivity

The chemoselectivity of the catalyst in the tandem reaction has been investigated. To do this, the equal molar concentration of the ketone (acetophenone dimethyl acetal) and the aldehyde (benzaldehyde dimethyl acetal) was reacted with ethyl cyanoacetate in the optimum conditions. As can be seen in Scheme 3, the acid–base bifunctional catalyst distinguishes between the aldehyde and the ketone with a high chemoselectivity with a 75% yield in 85 min. The confide space of mesoporous carbon CMK-3 may avoid the ketone from entering the mesostructured CMK-3, and subsequently, no further interaction happens between the ketone and acid–base sites of the catalyst [32, 74] (Table 5).

	OMe			
		ly(SSA-co-4VP)/CMK-3 ► x	C≡N ≻−C=C	+ H₂O
	x	H ₂ O / 60 °C	Ŭ Č-OEt	L
Entry	Substrate	Product	Yield (%) ^b	Time (min)
1	MeO_OMe	G − C − C − C − C − C − C − C − C − C −	87	75
2	MeO NO ₂	$O_2N - C = C CN - C = C CN - OEt OC C - OET OC - OET OC C - OET OC OC C - OET OC C - OET OC C - OET OC OC OC OC OC C - OET OC $	82	50
3	MeO OMe	$Br - \underbrace{ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	87	70
4	MeO OMe	Br C=C ^{CN} Br	86	75
5	MeO OMe		84	55
6	MeO OMe	$H_3CO - C - C - C - C - C - OEt$	82	80
7		HO-C=CCN H=CCCOEt	77	105

 $\label{eq:table_$

 aReaction conditions: catalyst (0.1 g), aromatic dimethyl acetal (1.87 mmol), ethyl cyanoacetate (1.87 mmol), H_2O (4 mL), 60 $^\circ C$

^bIsolated yield



Scheme 3 Chemoselectivity survey in the presence of the benzaldehyde dimethyl acetal and (1,1-dimethoxyethyl)benzene

 Table 5
 Deacetalization-Knoevenagel condensation reaction of aromatic dimethyl acetal with ethyl cyanoacetate using different materials



Entry	Catalyst	Solvent	<i>T</i> (°C)	Time (h)	Con. (%)	Yield (%)	Ref.
1	H-mont-NH ₂	Heptane	60	1	99	95	[64]
2	SO ₃ H-MCM-41-NH ₂	Benzene	80	0.5	100	95	[65]
3	SO ₃ H–NH ₂ –HMS	Benzene	80	0.5	100	94	[23]
4	AB-MCM-41-g	Toluene	80	1	100	96	[66]
5	MIL-101(Al)-NH ₂	1,4-dioxane	90	3	100	94	[67]
6	LZSM-5-AT-OH	Water/acetoni- trile	80	15	-	91	[68]
7	ZIF8-A61-SO ₃ H	1,4-Dioxane	80	4	100	98	[69]
8	P(DVB-NH ₂ -0.2-StSO ₃ H)	Toluene	80	24	100	99	[70]
9	Yb-BCD-NH ₂	DMSO	50	24	97	97	[71]
10	MOF-cd	DMF	90	5	-	95	[72]
11	Fe ₃ O ₄ @Cu-HKUST-1	1,4-dioxane	90	5	-	99	[73]
12	Ni-Pd@poly (SSA-NVI)/ KIT-6	Water	45	1.5	-	90	[58]
13	S-HPDVB@PBM-1	Toluene	80	0.5	99	99	[60]
14	MIL-101(Al/Fe)-NH ₂	Toluene	90	1.5	100	100	[57]
15	MONNs-SO ₃ H-NH ₂	Toluene	80	2	99	99	[35]
16	DMAN-SO ₃ H-OMS-5-5	Water	80	1	100	98	[18]
17	SO ₃ H-MONNs	Toluene	80	1.5	99	99	[20]
	NH ₂ -MONNs						
18	Acid-base-nanotube + PTSA	Water	r.t	24	95	95	[22]
19	$ZSM\text{-}5@Mg_3Si_4O_9(OH)_4$	Toluene	80	10	99	99	[9]
20	NH ₂ -SO ₃ H-H-ONTFs	Toluene	80	1	99	99	[8]
21	Poly(SSA-co-4VP)/CMK-3	Water	60	1.25	-	87	This report

Conclusion

In summary, the mesoporous carbon CMK-3 with a high surface area has been synthesized. Due to the mesoporous structure of the CMK-3 and its high surface area, the CMK-3 can be utilized as support to incorporate the acid–base copolymer (i.e., poly(SSA-co-4VP). Thanks to the good distribution of the copolymer into the mesopores of the CMK-3, the quenching of the acid and base sites of the polymers is minimized. The total amount of separated sites has been determined by almost 40% with the potentiometric titration method. The poly(SSA-co-4VP)/CMK-3 was utilized as the bifunctional acid–base catalyst in the tandem one-pot deprotection of deacetalization–Knoevenagel condensation reaction in aqueous media and in short reaction time. A profound comprehension of the conduct of acid and base sites in a solitary material will open the potentials of these kinds of materials toward tandem reactions, which is our prospect. Using mesomacroporous structured materials as support can facilitate a broad range of acid–base copolymerization within a highly accessible acid and base sites and utilizing them as the catalyst in tandem organic reactions.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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