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Short communication

Ultra-high concentrations of amino group functionalized nanoporous polymeric solid bases: Preparation, characterization and catalytic applications

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ABSTRACT

We report here that the amino-group functionalized nanoporous polydivinylbenzene (PDVB-2.0-NH_2, PDVB-NH_2), acts as an efficient solid base for catalyzing Knoevenagel condensation, which could be synthesized from nitration of nanoporous polydivinylbenzene (PDVB), reduction in the mixture containing $SnCl_2$ and HCl, and activated with isopropylamine. The resultant solid bases of PDVB-2.0-NH_2 and PDVB-NH_2 have large BET surface areas, abundant nanopores, controlled hydrophobic network and ultra-high concentrations of the amino group. The above characteristics result in their excellent activities and good recyclability for catalyzing Knoevenagel condensation of various aldehydes with malononitrile, much better than those of commercially basic resin of Amberlite-400 and Amberlite-910, which was as comparable as that of the homogeneously strong base of CaO. This work develops efficient nanoporous polymeric solid bases with controllable surface characteristics and ultra high concentrations of basic sites.

1. Introduction

Acid and base catalytic processes showed an inseparable relationship in the area of catalytic chemistry. In acid catalyzed reactions, reactants act as bases toward catalysts which act as acids. On the contrary, reactants act as acids toward catalysts in base catalyzed reactions [1], and acid and base catalyzed reactions have been paid much attention because of their wide applications for catalyzing production of various useful chemicals [1–11]. Compared with acid catalysis, base catalysis usually exhibits mild reaction conditions and high efficiency [6]. Typical base catalyzed reactions such as aldolization, alkylation, Knoevenagel, transesterification, glucose isomerization Michael condensations, and Wadsworth–Emmons additions are very efficient tools for the fabrication of various fine chemicals and biofuels in the industry [12,13]. Conventional base catalysts such as KOH, NaOH and CaO showed low cost, strong base strength, and excellent activities in various reactions, however, the drawbacks such as environmental concerns and difficult regeneration from reaction media largely constrain their wide applications [1].

In recent times, the replacement of homogeneous bases with solid bases for catalyzing production of fine chemicals and biofuels has received considerable attention [6,14–16]. Up to now, the common solid bases include alkaline earth oxides, basic zeolites, strong basic resins, clay minerals and hydrotalcite, which have been widely used in various base catalytic reactions, and showed relatively good catalytic activities [1,6,12,17]. However, their relatively low BET surface areas result in the low exposition degree of catalytically active sites and diffusion limitation of reactants in various reactions, which constrains their catalytic activities and lives [1,11,18–20]. Loading the basic active sites into highly porous supports such as zeolites, mesoporous silicas and porous carbons basically overcomes the poor porosity problems of conventional solid bases, and the resultant porous solid bases were active in various base catalyzed reactions such as Knoevenagel reactions, toward transesterification to biodiesel, and Michael addition etc. [1,15,21–24]. However, the reported porous solid bases showed the drawbacks including: (i) the limited contents of basic sites could be loaded into these porous materials and (ii) their sensitive basic sites could be easily poisoned by molecules such as H_2O and CO_2 because of their unique

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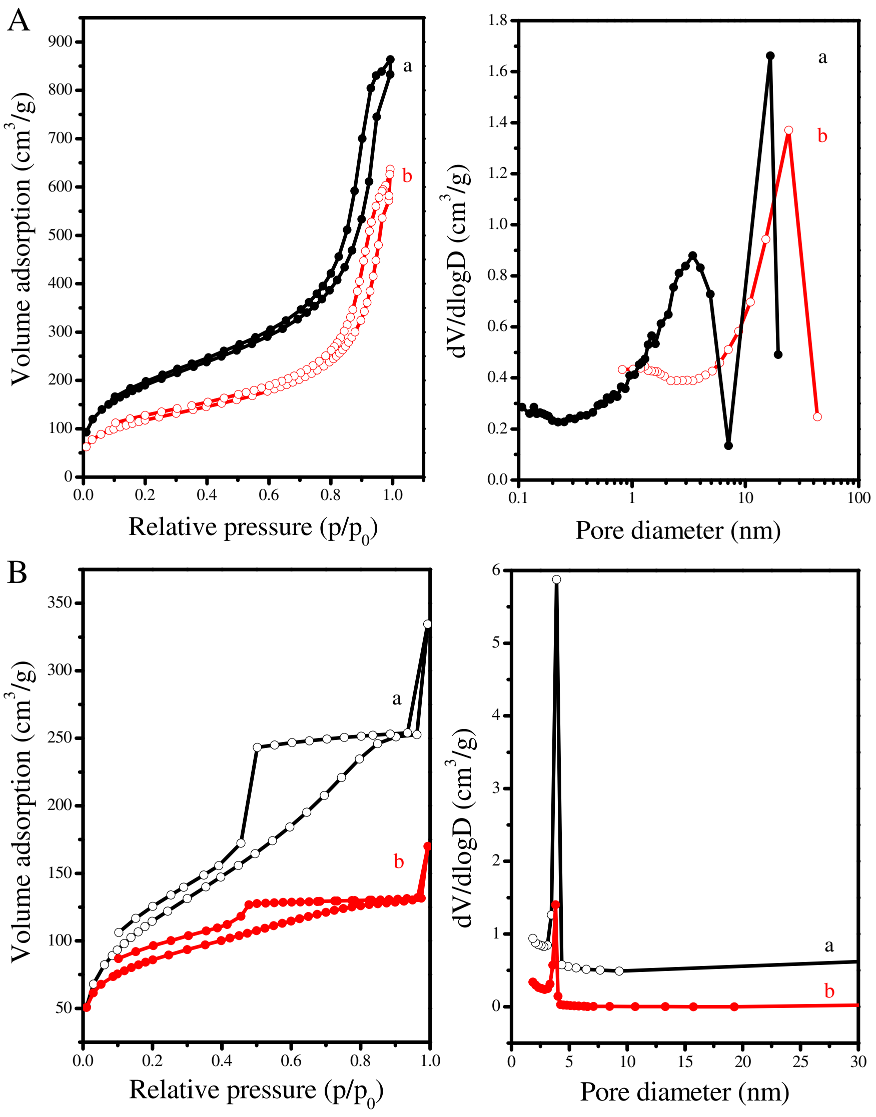


Fig. 1. N_2 isotherms and pore size distribution of (A) PDVB-2.0 and PDVB-2.0-NH_2, and (B) PDVB and PDVB-NH_2.

hydrophilic frameworks. The above problems found in reported solid bases strongly constrain their wide applications in various base-catalyzed reactions [1,6,25,26].

Up to now, it is still challengeable to synthesize porous solid bases with very high concentrations of basic sites and controllable hydrophobicity, which will be very important for the enhancement of catalytic activities and recyclability of solid base catalysts. Recently, our group successfully synthesized pyridine, imidazole and triazole functional, nanoporous polymeric solid bases, which showed very good hydrophobicity and controlled wettability for various organic reactants. These characters result in their very good stability in the air and good catalytic activity in various reactions [6,17]. However, the limited contents of basic sites that still constrain them are used as highly efficient solid bases in various reactions.

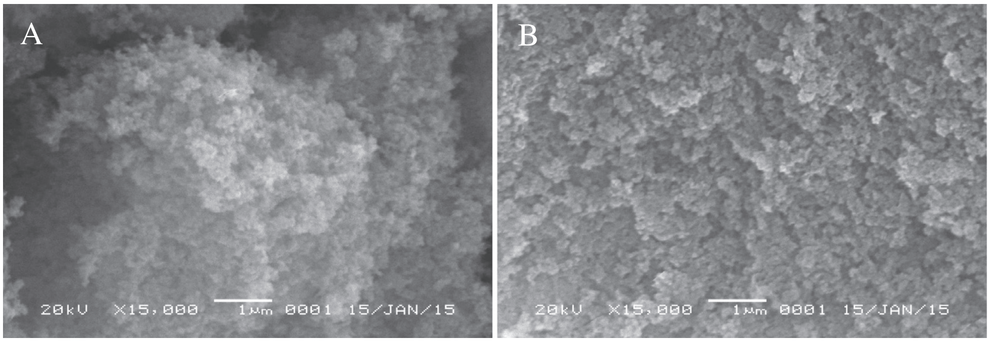


Fig. 2. SEM images of (A) PDVB-2.0-NH_2 and (B) PDVB-NH_2.

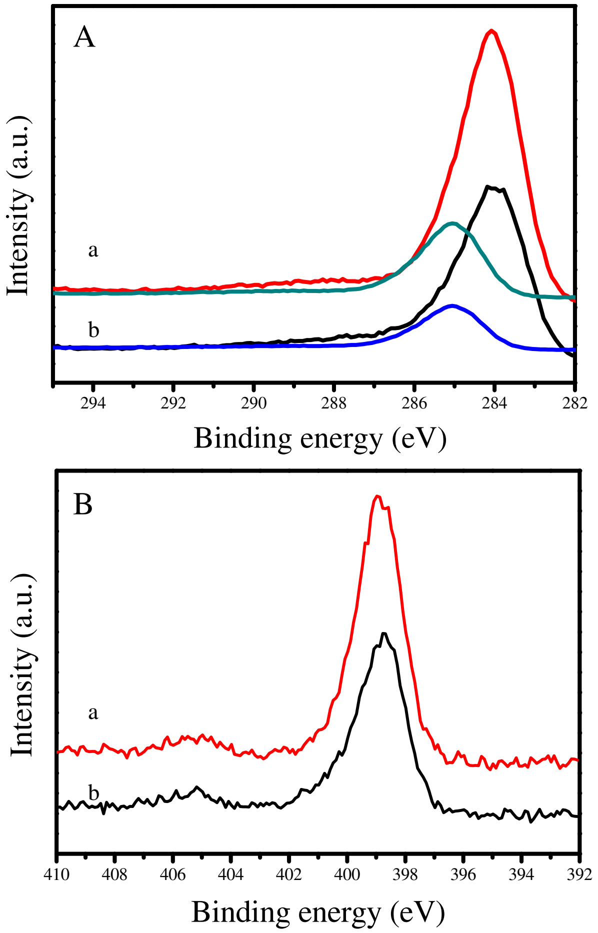


Fig. 3. XPS spectra of (A) C1s and (B) N1s of (a) PDVB-2.0-NH_2 and (b) PDVB-NH_2.

Herein, we report novel amino-group functionalized, superhydrophobic nanoporous polydivinylbenzene (PDVB-2.0-NH_2, PDVB-NH_2), which could be synthesized from nitration of superhydrophobic nanoporous polydivinylbenzene (PDVB), reduction in the mixture containing $SnCl_2$ and HCl, and activated with isopropylamine. The nanoporous PDVB support could be obtained through one-step solvothermal synthesis without using any organic templates. PDVB-NH_2 showed unique characteristics including large BET surface areas, good thermal stability, ultra-high concentrations of amino group, superhydrophobic network and controllable wettability for various organic substrates, which result in their good ability for anti-poison for H_2O and CO_2 in the air. The above characteristics make PDVB-2.0-NH_2 and PDVB-NH_2 show excellent catalytic activity and good recyclability in the reactions of Knoevenagel condensation, much better than those of conventional solid bases including conventional solid bases of Amberlite 400, Amberlite 910 and zeolite L, which was as comparable as that of homogeneous CaO. The preparation of PDVB-2.0-NH_2 and PDVB-NH_2 will develop a new way to the synthesis of nanoporous polymer based solid bases with controllable hydrophobicity, ultrahigh contents of basic sites, which will be very important for them used as highly efficient solid base catalysts in various base catalyzed reactions.

2. Experimental section

2.1. Synthesis of PDVB-2.0-NH_2 and PDVB-NH_2

PDVB-NH_2 and PDVB-2.0-NH_2 were synthesized from nitration of PDVB, reduction in the mixture containing $SnCl_2$ and HCl, and activated with isopropylamine (As shown in Scheme S1). Typically, 1.5 g of PDVB or PDVB-2.0 powder was added into a mixture containing 61.8 g of H_2SO_4 and 13.88 g of HNO_3 under ice bath condition, after stirring of the mixture for 72 h under vigorous stirring. Then, the reaction mixture was diluted with 800 mL of H_2O, the resultant PDVB-NO_2 could be obtained from filtration, washing with a large amount of water and drying at 60 °C under vacuum condition. To synthesize PDVB-NH_2, PDVB-NO_2 was dispersed into a mixture containing 6.4 g of $SnCl_2$ and 60 mL of HCl, after stirring the mixture at room temperature for 72 h, which was dispersed into 800 mL of water, filtration, washing with large amount of water and drying at 60 °C under vacuum condition. Then, the dried sample was activated with a mixture containing 20 mL of isopropylamine and 150 mL of ethanol for 30 min at room temperature. PDVB-NH_2 could be obtained from repeating this treatment for two times and drying at 60 °C under vacuum condition.

2.2. Catalytic reactions

The Knoevenagel condensation of benzaldehyde with malononitrile was performed in a flask equipped with a reflux condenser and magnetic stirrer. Typically, 2 mmol of aldehydes (benzaldehyde, cyclohexanone, 4-nitrobenzaldehyde, salicylaldehyde or furfural) and 2 mmol of malononitrile were dispersed into 5 mL of ethanol solvent, then 0.02 g of catalyst was rapidly added. After stirring of the mixture at 80 °C for 2 h, the reaction was finished. The products were analyzed by using gas chromatography systems (Agilent 7890) with a flame ionization detector (FID). The initial temperature of the column was 100 °C, ramping rate was 20 °C/min, and the final temperature was 280 °C; the temperatures of the inlet and detector were 300 and 350 °C, respectively. In this reaction, the concentrations of products were calculated through the internal standard (dodecane) method. In the meanwhile, the catalysts could be regenerated from centrifugation, washing with large amount of ethanol, reactivated with isopropylamine and drying at 60 °C. The regenerated catalyst was directly used for the next run.

3. Results and discussion

Fig. 1 showed N_2 isotherms and pore size distribution of nanoporous PDVB, PDVB-2.0, PDVB-NH_2 and PDVB-2.0-NH_2. All of these samples showed typical IV adsorption curves. For the samples of PDVB-2.0 and PDVB-2.0-NH_2, which gave the sharp capillary condensation step at relative pressure $P/P_0 = 0.85–1.0$. Meanwhile, PDVB and PDVB-NH_2 gave the sharp capillary condensation step $P/P_0 = 0.4–0.7$. These results indicate the formation of abundant nanopores in these samples. Correspondingly, the pore sizes of PDVB-2.0 and PDVB-2.0-NH_2 were centered at 3.5 & 16.3 and 24.1 nm (Fig. 1A), and the pore sizes of PDVB and PDVB-NH_2 were centered at 3.85 and 3.83 nm (Fig. 1B). Compared with PDVB and PDVB-2.0 (460 and 700 m^2/g), the decreased BET surface areas in PDVB-NH_2 and PDVB-2.0-NH_2 (186 and 429 m^2/g, Table S1) should be resulted from the grafting of amino group in PDVB and PDVB-2.0 supports, which largely increase the weight of their network, similar results have also been reported previously [27]. Compared with PDVB, the decreased volume adsorption could not be observed in PDVB-NH_2 in microporous region, which may be attributed to decomposition of unstable units such as oligomers during nitration and reduction processes. Alternatively, the decomposition of unstable units leads to the enlarged pore diameter in PDVB-2.0-NH_2 (Fig. 1B). The different structural changes in PDVB-2.0-NH_2 and PDVB-NH_2 may be attributed to their obviously different nanoporous structures and cross linking degree of their supports. On the other hand, the concentrations of nitrogen (basic site) in PDVB-NH_2 and PDVB-2.0-NH_2 were 10.1 and 10.8 mmol/g respectively, which was much higher than those of commercial basic resin of Amberlite 400 (5.18 mmol/g), Amberlite IRA910 (3.5 mmol/g) and reported sold bases [15,21,28].

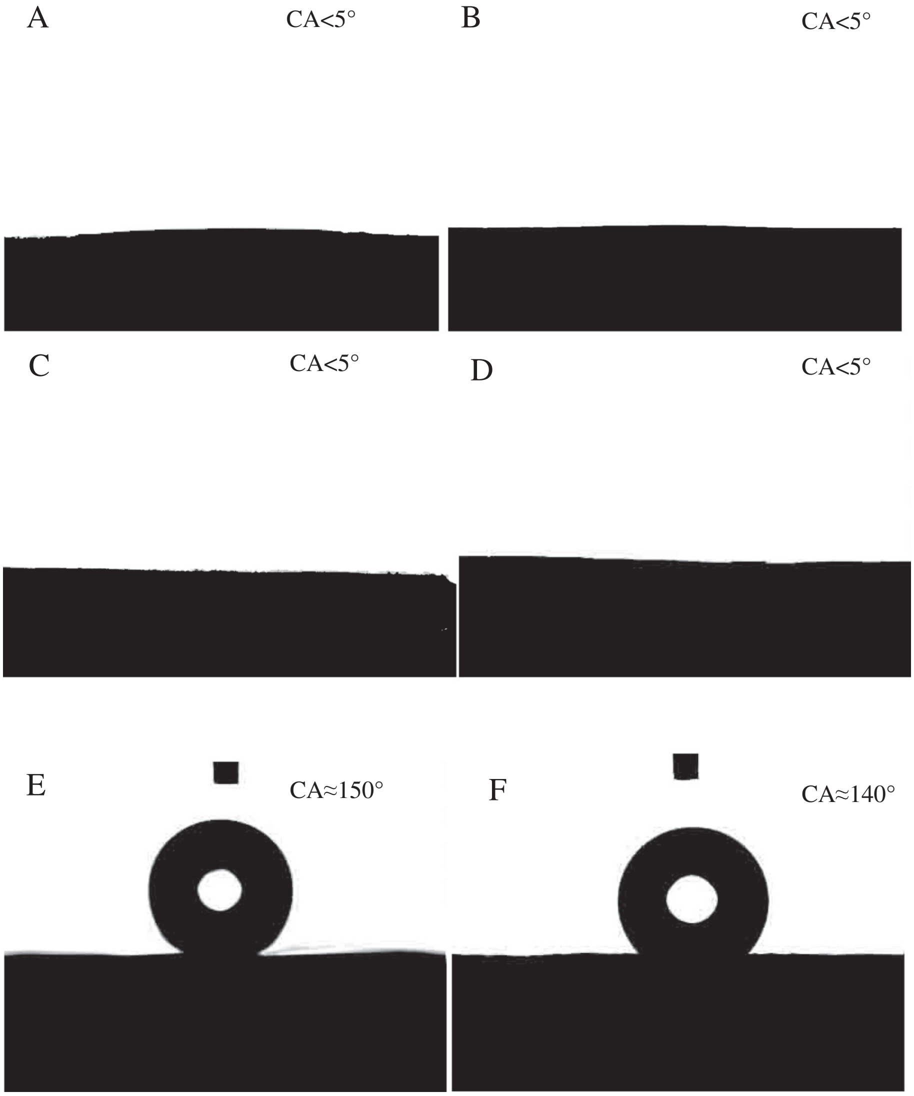


Fig. 4. Contact angles of a malononitrile droplet on (A) PDVB-2.0-NH_2 and (B) PDVB-NH_2, a benzaldehyde droplet on (C) PDVB-2.0-NH_2 and (D) PDVB-NH_2, and A water droplet on (E) PDVB-2.0-NH_2 and (F) PDVB-NH_2.

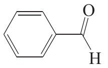
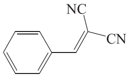
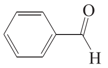
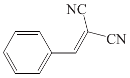
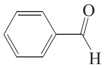
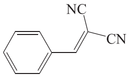
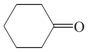
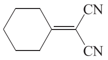
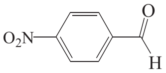
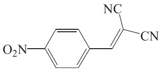
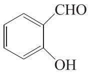
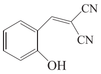
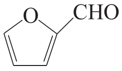
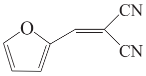
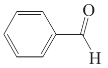
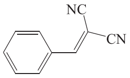
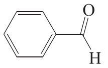
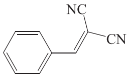
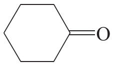
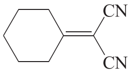
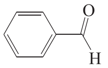
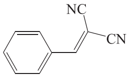
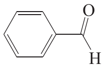
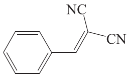
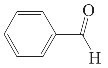
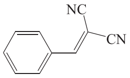
Fig. 2 showed SEM images of PDVB-2.0-NH_2 and PDVB-NH_2, which is an efficient technique to determine the surface characteristics of various nanomaterials. Notably, PDVB-2.0-NH_2 and PDVB-NH_2 showed rough surface with sponge-like structures, which exhibited abundant porosity with nanoscaled pore diameters, in agreement with the result obtained from N_2 isotherms and TEM results (Fig. S1). Abundant nanoporosity was favorable for the decreasing of diffusion limitation of various organic substrates in these samples [6].

Fig. 3 showed XPS spectra of PDVB-NH_2 and PDVB-2.0-NH_2. Notably, the peaks associated with C_{1s} (284.8 eV) and N_{1s} (402.1 eV) could be clearly observed in these samples. Furthermore, the broaden C_{1s} spectra could be fitted and deconvoluted into two peaks, centered at around 284.8 and 286.1 eV, which should be assigned to C—C and C—N bonds in these samples [28]. Correspondingly, the N_{1s} spectrum could also be fitted and deconvoluted into two peaks centered at around 398.4 and 401.8 eV, which may be attributed to —NH_2 and partial oxidation of —NH_2 on the surface of the samples. These results confirm the successful grafting of —NH_2 group onto the network of PDVB and PDVB-2.0, in agreement with FT-IR and ^{13}C NMR results (Figs. S2&3) [28].

Fig. 4 showed contact angle of PDVB-2.0 and PDVB for water, and PDVB-2.0-NH_2 and PDVB-NH_2 for malononitrile and benzaldehyde. Notably, PDVB-2.0 support gives the contact angle up to 150° for water, which indicates its superhydrophobic surface characteristics. Alternatively, PDVB-2.0-NH_2 shows the contact angles lower than 5° for both malononitrile and benzaldehyde, which indicate its superwettability for these organic substrates. Similar results could also be found in the samples of PDVB and PDVB-NH_2. The unique hydrophobic network in PDVB-2.0-NH_2 and PDVB-NH_2 was favorable for enhancement of its anti-poison ability for H_2O and CO_2 during various base catalyzed reactions [6]. On the other hand, their superwettability for malononitrile and benzaldehyde largely decreases the diffusion limitation of the reactants in the samples, further resulting in their enhanced exposure degree of catalytically active sites [6], which largely improves its catalytic activity for conversion of these substrates through Knoevenagel condensation.

Table 1 presents catalytic performances of various catalysts in Knoevenagel condensation. Notably, both PDVB-2.0-NH_2 and PDVB-NH_2 were very active for catalyzing Knoevenagel condensation of malononitrile with benzaldehyde (Table 1 Runs 1 & 3), much higher than those of basic resins of Amberlite 400, Amberlite 910 amino group functionalized ordered mesoporous silica (OMS-NH_2) and zeolie L (Table 1, Runs 8–12), which were as comparable as that of homogeneous base of CaO (Table 1, Run 13). For example, in the reaction of malononitrile with benzaldehyde, the product yield catalyzed by PDVB-2.0-NH_2 and PDVB-NH_2 were up to 99.1 and 98.6% only after

Table 1
Catalytic data in Knoevenagel condensation over various samples.[a]

Run	Catalysts	Substrates	Products (sel. %)		Conv. (%)	TOF (h^{-1}) [d]
1	PDVB-2.0-NH_2			>99.0	99.1	4.6
2	PDVB-2.0-NH_2 [b]			>99.0	95.3	4.6
3	PDVB-NH_2			>99.0	98.6	4.9
4	PDVB-2.0-NH_2			>99.0	95.6	4.4
5	PDVB-2.0-NH_2			>99.0	90.5	4.2
6	PDVB-2.0-NH_2			>99.0	89.3	4.1
7	PDVB-2.0-NH_2			>99.0	96.8	4.5
8	Amberlite 400 (OH form)			>99.0	75.2	7.3
9	Amberlite 910 (OH form)			>99.0	86.3	11.7
10	Amberlite 910 (OH form)			>99.0	81.9	11.1
11	Zeolite L			>99.0	75.7	–
12	OMS-NH_2 [c]			>99.0	86.4	36.0
13	CaO			>99.0	99.2	2.8

[a] Reaction conditions: 2 mmol of aldehydes, 2 mmol of malononitrile, 5 mL of ethanol solvent, and 0.02 g of catalyst. Reaction temperature: 80 °C. Reaction time: 2 h. The products were analyzed by using gas chromatography systems (Agilent 7890) with a flame ionization detector (FID). The conversions of various reactants were determined by using internal standard (n-dodecane) method.

[b] The catalyst has been recycled for 5 times.

[c] Typical mesoporous solid bases synthesized as in Ref. [27].

[d] Turn over frequency.

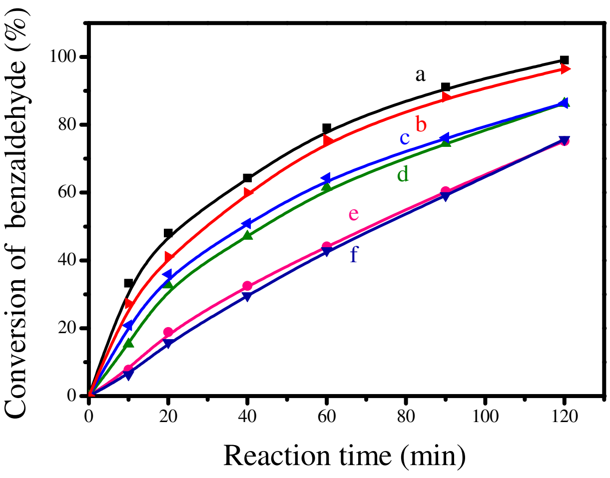


Fig. 5. Dependences of catalytic activities on the time in Knoevenagel condensation of benzaldehyde with malononitrile catalyzed by (a) PDVB-2.0-NH_2, (b) PDVB-2.0-NH_2 recycled for 5 times, (c) Amberlite 910, (d) OMS-NH_2, (e) Zeolite L and (f) Amberlite 400.

reacting for 2 h, which showed very good selectivity (>99%). On the contrary, the product yields catalyzed by Amberlite 400, Amberlite 910, zeolite L and OMS-NH_2 were only 75.2, 86.3, 75.7 and 86.4%, respectively. The product yield catalyzed by strongly homogeneous CaO was 99.2%, similar with those of PDVB-2.0-NH_2 and PDVB-NH_2. More importantly, PDVB-2.0-NH_2 showed good reusability, even after being reused for 5 times, the regenerated PDVB-2.0-NH_2 still gave superior activity (Table 1, Run 2), which was as comparable as that of fresh PDVB-2.0-NH_2 (Table 1, Run 1). Correspondingly, the dependences of catalytic activities on reaction time in Knoevenagel condensation of benzaldehyde with malononitrile catalyzed by various catalysts have also been investigated in Fig. 5, which further confirms very good activity and reusability of PDVB-2.0-NH_2 and PDVB-NH_2 in comparison with those of Amberlite 910, OMS-NH_2, Zeolite L and Amberlite 400, in good agreement with the results obtained in Table 1. Meanwhile, their high activities could also be expanded to other substrates, which include the reactions of malononitrile with other substrates such as cyclohexanone, *p*-nitrobenzaldehyde, salicylaldehyde and furfural (Table 1 Runs 4–7).

Compared with Amberlite 400, Amberlite 910, the better catalytic activities found in PDVB-2.0-NH_2 and PDVB-NH_2 should be attributed to their large BET surface areas, controllable hydrophobicity and wettability for the reactants (as shown in Fig. 4), and ultra high concentrations of amino groups, which largely increase the exposure degree of catalytically active sites. Alternatively, a relatively lower activity of zeolie L should be attributed to its constrained micropores, which results in the difficult accessibility of bulky substrates to catalytically active sites. On the other hand, the hydrophilic framework and low concentration of basic site of OMS-NH_2 result in its lower activity in comparison with those of PDVB-2.0-NH_2 and PDVB-NH_2 [6,20]. It is noteworthy that PDVB-2.0-NH_2 and PDVB-NH_2 showed relatively lower TOF values (Table 1), which should be attributed to their ultra-high concentrations of basic sites in comparison with various solid bases (Table S1). For instance, the TOF value of OMS-NH_2 (36.0) was higher than that of PDVB-2.0-NH_2 (4.6) in Knoevenagel condensation of malononitrile with benzaldehyde, however, its relatively lower activity (Table 1) that largely constrains it is used as efficient solid base in various base-catalyzed reactions in industry. The preparation of PDVB-2.0-NH_2 and PDVB-NH_2 will develop novel and efficient solid bases for catalyzing C—C bond formation through Knoevenagel condensation.

4. Conclusion

Novel nanoporous polymeric solid bases of PDVB-2.0-NH_2 and PDVB-NH_2 with ultra high concentrations of basic sites, large BET surface areas, and controllable surface characteristics have been prepared in this work. The resultant PDVB-2.0-NH_2 and PDVB-NH_2 showed excellent catalytic activities and recyclability in Knoevenagel condensation in comparison with various conventional solid bases. The preparation of PDVB-2.0-NH_2 and PDVB-NH_2 will develop a new way to synthesize highly efficient nanoporous solid bases, which will be very important for their wide applications for catalyzing production of various useful chemicals through green and sustainable base-catalyzed processes.

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Appendix A. Supplementary data

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