Catalysis Communications 12 (2011) 1212–1217

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Homogeneous-like solid base catalysts based on pyridine-functionalized swelling porous polymers

Yong-Lai Zhang [a,*], Sen Liu [c], Siyu Liu [c], Fujian Liu [c], Haiyan Zhang [c], Yinyan He [c], Feng-Shou Xiao [b,*]

[a] State Key Laboratory on Integrated Optoelectronics, Electronic Science and Engineering, Jilin University, Changchun 130012, China
[b] Department of Chemistry, Zhejiang University, Hangzhou, 310028, China
[c] College of Chemistry and State Key Laboratory of Inorganic synthesis and Preparative Chemistry, Jilin University, Changchun, 130012, China

ARTICLE INFO

Article history:
Received 1 March 2011
Received in revised form 13 April 2011
Accepted 17 April 2011
Available online 22 April 2011

Keywords:
Homogeneous-like
Base catalysts
Porous
Pyridine functionalized
Polymers
Swelling

ABSTRACT

Reported here is the synthesis of pyridine-functionalized porous polymers, which are designed as homogeneous-like base catalysts. These highly porous catalysts have adjustable pyridine contents, high BET surface area (312–649 m^2/g), large pore volume (0.5–2.0 cm^3/g) and rapid swelling property, thus they efficiently combined the advantage of both homogeneous and heterogeneous catalysts. The exposure degree of active sites in our homogeneous-like catalysts has been evaluated by Cu^{2+} adsorption, giving similar capacity with homogeneously dissolved poly-4-vinylpyridine. In the Knoevenagel condensation, these materials exhibit excellent activity and stability compared with Mg–Al hydrotalcite and magnesia as well as homogeneous base catalyst of poly-4-vinylpyridine.

1. Introduction

As the "protagonist" of chemical reactions, catalysts have been paid intensive attentions because they are usually concerned with materials, environment, energy, sustainability, and human life [1,2]. Homogeneous catalysts contribute sufficient contact of active sites with reactants, exhibiting excellent performance in a wide range of reactions [3,4]. However, they suffer from serious problems in separation and environmental pollutions, which hinder their industrial applications significantly [5]. On the contrary, heterogeneous catalysts have the advantages in separation, reusage, and environmental protection, but their relatively low exposure degree of active sites on the solid surface strongly influences their catalytic properties [6,7]. To overcome the drawbacks of these heterogeneous catalysts, nanoporous solids with high surface areas and large pore volume have been extensively used. For example, zeolites, mesoporous materials, and nanoporous polymers have been developed as efficient catalysts for a series of reactions [8–18]. However, either inorganic or organic porous solids are not as active as homogeneous catalysts due to the limitation of exposed active sites on the solid surface despite their high surface area and hierarchically porous structures [19–21]. As an alternative choice, phase-transfer catalysts have been successfully developed towards high activity [22,23]. Nevertheless, they still cannot be widely applied because of their reaction-controlled property. Therefore, it is still a challenging task to develop novel catalysts that could combine the advantages of both homogeneous and heterogeneous catalysts in a controlled fashion.

Recently, we have reported surperhydrophobic nanoporous polymers with swelling property, which exhibit outstanding adsorptive capability for organic compounds [24]. In fact, the combination of swelling property and porous structure imparts homogeneous-like performance to these unique polymer-based materials when they are used in organic solvents. Here we demonstrated a synthesis of pyridine-functionalized porous polymers, which have high BET surface area, large pore volume, adjustable pyridine contents, and swelling property. Based on these unique properties, they are designed as novel homogeneous-like base catalysts for organic phase catalytic reactions. Before catalytic activity evaluation, the exposure of active sites (pyridine groups) was measured through Cu^{2+} adsorption in organic solvents. In the Knoevenagel condensation, a representative base-catalyzed reaction, these materials exhibit high activities and stability as compared with conventional solid base catalysts.

2. Experimental

2.1. Synthesis

In a typical synthesis of swelling porous poly-divinylbenzene and poly-4-vinylpyridine copolymer, 2 g of the mixture composed of divinylbenzene (DVB) and various amount of 4-vinylpyridine (VP) was dissolved in ethyl acetate (20 mL), followed by addition of

---

* Corresponding authors. Tel.: +86 431 85168590; fax: +86 431 85168624.
E-mail addresses: yonglaizhang@jlu.edu.cn (Y.-L. Zhang), fsxiao@mail.jlu.edu.cn (F.-S. Xiao).

1566-7367/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2011.04.020

azobisisobutyronitrile (AIBN, 0.05 g). After stirring at room temperature for 5 h, the resulting mixture was transferred into an autoclave and aged for 24 h at 100 °C. After evaporation of the solvents at room temperature for 48 h, a solid monolith was finally obtained. The products were designated as PDVB-VP-*n*, where *n* stands for the percentage of VP in the two monomers ($n=5$, 10, 20, and 30). Polydivinylbenzene (PDVB) was prepared in the same way without the addition of 4-vinylpyridine. Poly-4-vinylpyridine (PVP) was prepared by thermal polymerization of VP without using solvents.

For comparison, Mg–Al hydrotalcite was prepared according to published literature [25] and calcined in air at 600 °C for 6 h. The Mg–Al hydrotalcite was activated by water treatment at 30 °C. Magnesium oxide was purchased from Tianjin-Guangfu Chemical Company. For activation, MgO sample was treated at 600 °C in air for 30 min.

2.2. Knoevenagel condensation

The liquid-phase Knoevenagel condensation of various aldehydes with malononitrile was performed in a flask equipped with a reflux condenser and a magnetic stirrer. In a typical experiment, 2 mmol of benzaldehyde, 2 mmol of malononitrile and 5 mL of cyclohexane were stirred at 40 °C, and then 0.02 g of fresh catalyst (0.004 g for PVP) was rapidly added to start the reaction. Dodecane was used as an internal standard. After the reaction at 40 °C for 2 h, the products were analyzed by gas chromatography (GC-14C, Shimadzu) with a FID detector. The reaction cycles were carried out using PDVB-VP-20 catalyst with the procedure outlined above. After each cycle the catalyst was separated, washed with ethanol and dried at 60 °C for 12 h.

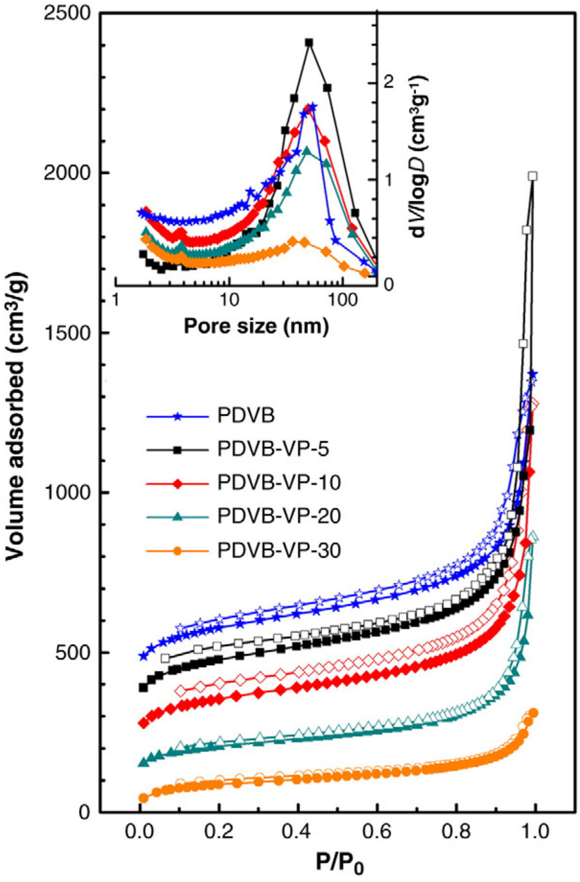


Fig. 1. Nitrogen isotherms and pore size distributions of PDVB-VP-*n* samples and pure PDVB sample. Isotherms of PDVB-VP-10, PDVB-VP-20, PDVB-VP-30, and PDVB have been offset by 100, 200, 300, 400 cm^3/g respectively, along the vertical axis for clarity.

Table 1
Textural parameters of porous polymers.

Samples	N content[a] (wt%)	S_{BET} (m^2/g)	V_p (cm^3/g)	D_p (nm)
PDVB-VP-5	0.66	649	2.0	51
PDVB-VP-10	1.29	567	1.6	50
PDVB-VP-20	2.34	406	1.2	48
PDVB-VP-20[b]	2.34	386	1.2	48
PDVB-VP-30	3.31	312	0.5	46
PDVB	0	676	1.4	50

S_{BET}: BET surface area of the samples.
V_p: total pore volume of the samples.
D_p: average pore diameter of the samples.
[a] Experimental N content was calculated by CHN elemental analyses.
[b] The sample was tested after the 5th use.

2.3. Adsorptive experiments

20 mg for PVP and 100 mg for PDVB-VP-20 (20% of VP) were added into 10 mL of Cu^{2+} solution, respectively. After stirring for 12 h at room temperature, the liquids were separated by ultrafiltration membrane for further titration.

For preparation of saturated Cu^{2+} solutions, 1 g $Cu(CH_3COO)_2 \cdot H_2O$ was added into 100 mL of ethanol under stirring for 1 h for further usage.

In the preparation for titration solution, 6.72 g of ethylenediaminetetraacetic acid disodium salt was dissolved in 1000 mL of water, which was further titrated by $CaCl_2$ solution prepared by HCl and required amount of $CaCO_3$. The buffer solution ($pH=3.5$) was prepared by mixing 250 mL 2 mol/L $ClCH_2COOH$ solution and 500 mL of NaAc solution (1 mol/L). Indicator was 0.3 wt.% 1-(2-pyridylazo)-2-naphthol (PAN) in ethanol.

2.4. Characterization

Nitrogen isotherms were obtained at −196 °C on a Micromeritics Tri-star 3000 analyzer. Samples were normally prepared for measurement by treating at 150 °C under nitrogen atmosphere for 12 h. Pore size distributions were calculated using Barrett–Joyner–Halenda (BJH) method. TEM experiments were performed on a Philips CM 200 LaB6

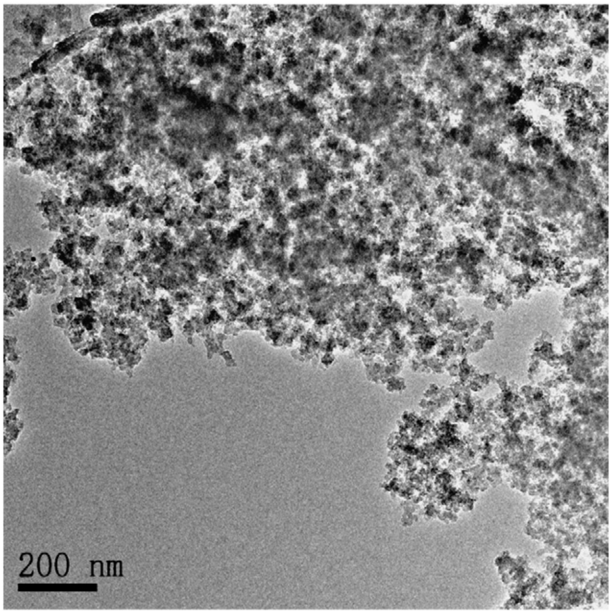


Fig. 2. TEM image of PDVB-VP-20 sample.

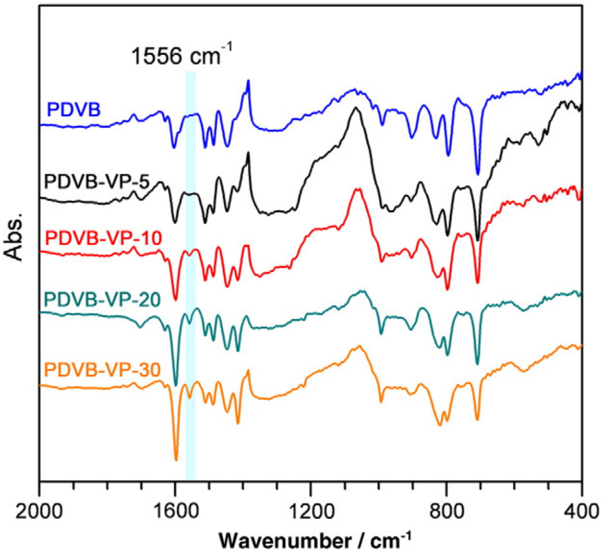


Fig. 3. FT-IR spectra of PDVB-VP-*n* and pure PDVB samples. Form top, they are pure PDVB, PDVB-VP-5, PDVB-VP-10, PDVB-VP-20 and PDVB-VP-30, respectively.

transmission electron microscope. Fourier transform infrared (FTIR) spectroscopy was performed on Nicolet Impact 410 infrared spectrometer in the range 400–4000 cm^{-1} using KBr pellets. The thermogravimetric analyses (TGA) were obtained in air with a Perkin-Elemer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min. CHN elemental analyses were performed on an Elemental Analyses MOD-1106. ^{13}C NMR MAS spectrum was recorded on a Bruker AVANCE III 400 WB spectrometer. SEM image was measured on a JEOL JSM-6700F field emission scanning electron microscope.

3. Results and discussion

Fig. 1 shows N_2 isotherms of poly-divinylbenzene and poly-4-vinylpyridine copolymers (PDVB-VP-*n*, where *n* stands for the mass percentage of 4-vinylpyridine in the two monomers), and PDVB sample for comparison. Notably, all the samples exhibit obvious nitrogen uptakes at a high relative pressure of 0.8–1.0, indicating the presence of large mesopores and macropores. Correspondingly, pore size distributions (inset of Fig. 1) are ranged at 20–100 nm, indicating the presence of both mesopores and macropores. Their textural parameters are presented in Table 1. Pure PDVB shows a high BET surface area of 676 m^2/g, indicating its porosity. For copolymer samples, PDVB-VP-5 also has a large BET surface area of 649 m^2/g and a pore volume of 2.0 cm^3/g. For synthesis of these porous polymeric catalysts, the active component of 4-vinylpyridine (VP) could be adjusted in a controlled manner. Through careful investigation of the textural parameters of samples with different VP contents, we found that the increase of VP in the polymers would result in a significant decrease of surface area and pore volume. As shown in Table 1, PDVB-VP-10, PDVB-VP-20 and PDVB-VP-30 have BET surface area of 567, 386, 312 m^2/g, and pore volumes of 1.6, 1.2, 0.5 cm^3/g, respectively.

As a typical example, TEM image of PDVB-VP-20 is shown in Fig. 2. Obviously, the sample is highly porous. Disordered mesopores could be identified all over the sample. The pore size is about 20–100 nm, in good agreement with the results estimated from N_2 isotherms.

FTIR spectra of PDVB-VP-*n* samples show the band at 1556 cm^{-1} associated with C–N stretching frequency, indicating the presence of pyridine groups (Fig. 3). The peak intensity increases with the amount of 4-vinylpyridine in the starting monomers, which indicates the adjustable pyridine groups contents in the final samples. Furthermore, ^{13}C NMR spectrum of PDVB-VP-20 sample confirms the presence of pyridine groups in the sample (Fig. S1). In our experiments, nitrogen content in the polymer samples was calculated by CHN elemental analyses. As shown in Table 1, N content could be adjusted in the

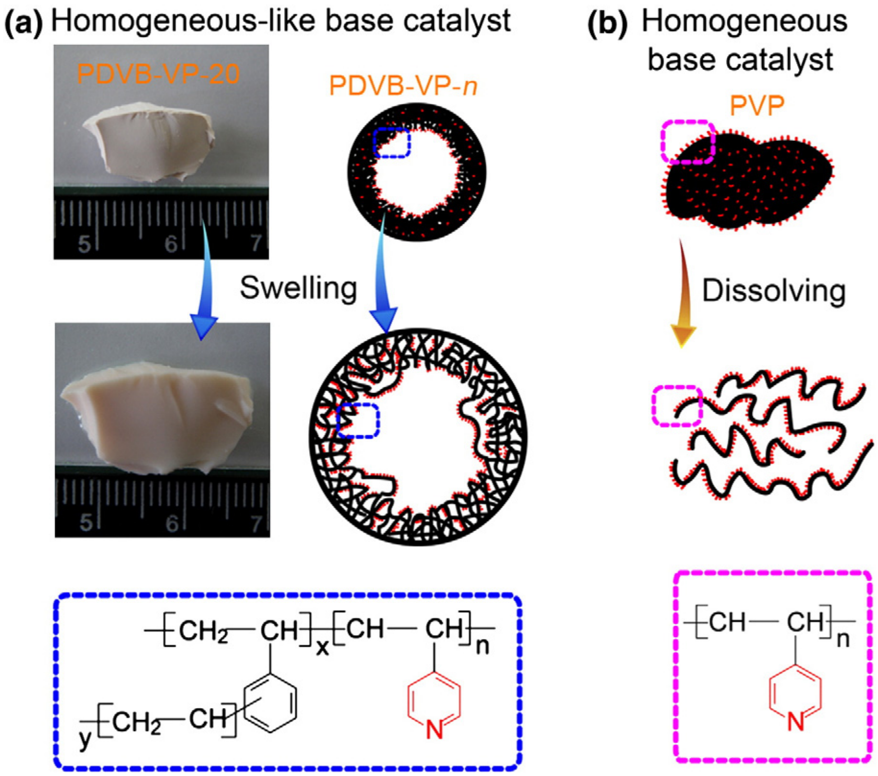


Fig. 4. Scheme for swelling property of (a) PDVB-VP-*n* samples which are designed as homogeneous-like base catalysts, and dissolving property of (b) PVP sample which is homogeneous base catalyst.

range of 0.66–3.31% by changing the percentage of 4-vinylpyridine and divinylbenzene in the starting monomers.

Thermal stabilities of these polymers are characterized by thermogravimetric (TG) curves (Fig. S2). Significant weight loss for PDVB-VP-5 and PDVB-VP-30 starts from 380 °C, indicating their excellent thermal stabilities. The amount of VP does not show any influence on their thermal stabilities.

Fig. 4a shows photos of PDVB-VP-20 monolith before and after swelling in cyclohexane. Clearly, the introduction of cyclohexane drops leads to a rapid expansion in the sample volume (3.5 times of volume larger than dry sample). Since the synthesis of the polymer was carried out in the presence of plenty of organic solvents under solvothermal condition, a loose porous network was formed after removal of the solvents, giving the possibility for swelling as a reversible process [24]. This unique swelling property would impart these polymers a promising feature for catalytic application. When they are used as catalysts in organic solvents, active sites in these highly swelled nanostructures would be completely exposed to reactants, just like homogeneous catalysts (Fig. 4b). It is worthy pointing out that the swelling property is not limited to cyclohexane, it works in various organic solvents. Fig. S3 shows the morphology change in a series of organic solvents. The volume change (the volume ratio of swelling sample to dry one) of PDVB-VP-20 sample is in the range of 2.5 to 3.5 (Supporting information, Table S1). For recycling usage, these swelling solid could also be easily separated from the solvent, whereas the homogeneous catalysts which are dissolved in the solvent would suffer from complex separation procedures. Apparently, this kind of polymers effectively combines the advantages of both highly exposed active sites for homogeneous catalysts and easy recycles for heterogeneous catalysts together.

To understand the exposure degree of pyridine groups in organic solvents, the interaction of pyridine groups in both PDVB-VP-20 and poly-4-vinylpyridine (PVP) with Cu^{2+} cations has been investigated [26,27]. PVP could be homogeneously dissolved in ethanol, where each of pyridine groups was exposed. After interacting with Cu^{2+} cations, a blue PVP solution is formed (Fig. 5a). In contrast, swelling porous PDVB-VP-20 in ethanol also interacts with Cu^{2+} cations, giving light-green solid (Fig. 5a). Very interestingly, the saturated adsorption capacity for the two samples is almost the same. PDVB-VP-20 has a capacity of 0.80 mmol/g, which is almost the same as PVP (4.05 mmol/g), considering that the content of pyridine groups in PDVB-VP-20 is only 20% of that in PVP. These results suggest that each of pyridine groups in PDVB-VP-20 could interact with Cu^{2+} species, which is the character of homogeneous phase. In addition, as a typical example, the content of basic sites in PDVB-VP-20 was measured by acid–base titration. Experimental results show that basic sites in the sample is about 1.65 mmol/g, which is in agreement with the N content measured from CHN elemental analyses (Table 1).

Knoevenagel condensation catalyzed by base catalysts, a typical C–C coupling between aldehydes or ketones with methylene-based compounds, is of great importance for the synthesis of fine chemicals and pharmaceutically important molecules [13,14,28–30]. Fig. 5b shows catalytic yields of benzaldehyde with malononitrile in the solvent of cyclohexane over various catalysts. Notably, blank or pure PDVB sample

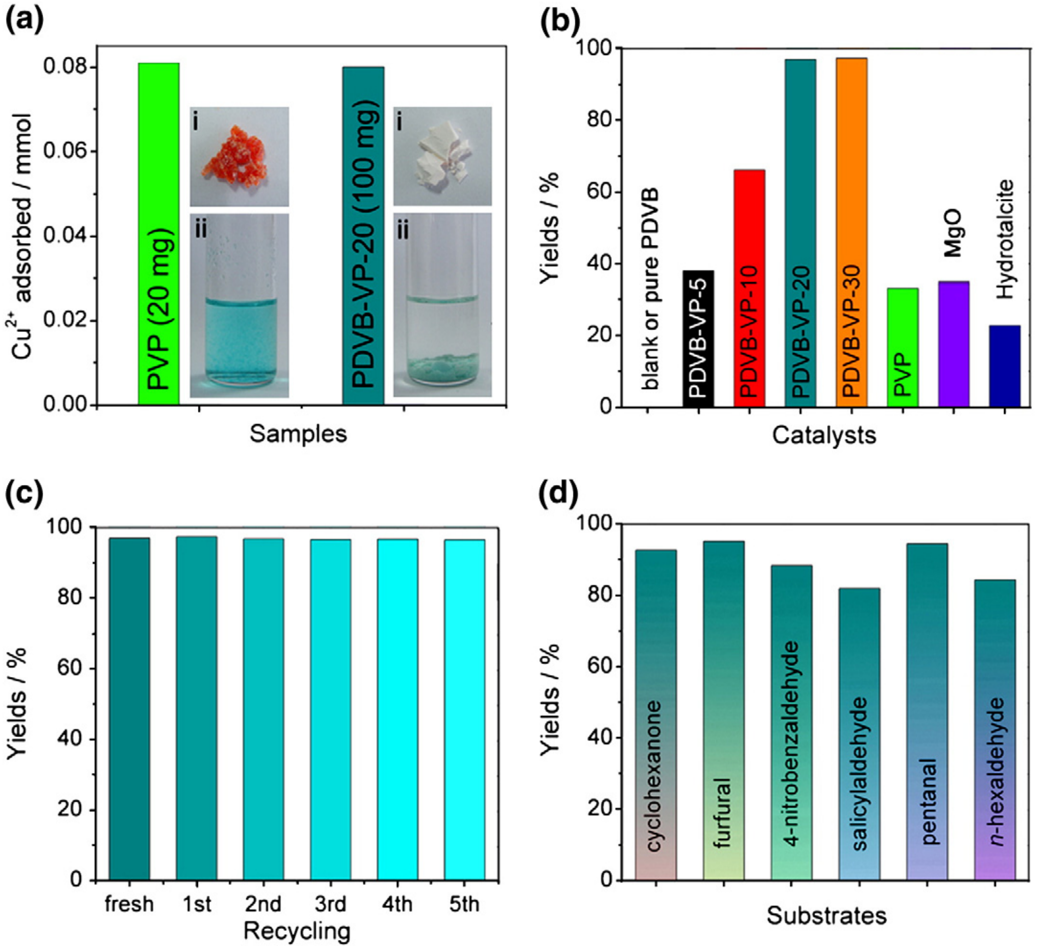
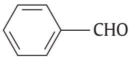
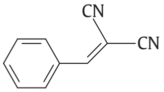
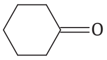
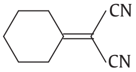
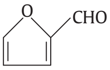
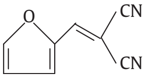
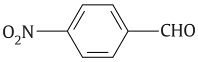
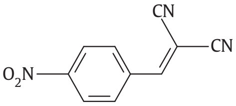
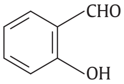
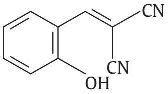
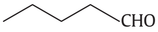
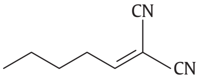
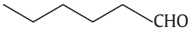
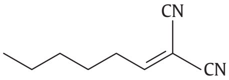


Fig. 5. The adsorption capacity of Cu^{2+} cations on PDVB-VP-20 and PVP (inset: photographs of adsorption process for PVP and PDVB-VP-20, i: fresh polymers; ii: polymers in Cu^{2+} solution) (b) Knoevenagel condensation over various catalysts, (substrate: benzaldehyde); (c) Recycles for PDVB-VP-20 catalyst, (substrate: benzaldehyde); (d) Knoevenagel condensation with various substrates over PDVB-VP-20.

Table 2
The charts of various substrates and corresponding Knoevenagel condensation products.

Run	Substrates		Products		Conversion (%)
1	benzaldehyde		2-(Benzylmethylene)malononitrile		97.0
2	Cyclohexanone		2-Cyclohexylidenemalononitrile		92.6
3	Furfural		2-(Furylmethylene)malononitrile		95.1
4	4-Nitrobenzaldehyde		2[(4-Nitrophenyl)methylene]malononitrile		88.3
5	Salicylaldehyde		2-[(2-Hydroxyphenyl)methylene]malononitrile		81.9
6	Pentanal		2-(Pentylmethylene)malononitrile		94.5
7	*n*-Hexaldehyde		2-(Hexylmethylene)malononitrile		84.3

is inactive to the reaction due to the absence of basic sites. Conventional solid base catalysts of magnesium oxide and Mg–Al hydrotalcite show the yields of 35.5% and 22.5% after activation. The relatively low conversion is attributed to their limitation of exposed active sites on the surface. However, PDVB-VP-*n* samples exhibit much higher yields (38–97%). Particularly, PDVB-VP-20 and PDVB-VP-30 give the yields of 97.0 and 97.1%. Kinetic studies show that when the reaction time reaches 120 min, all the samples give their highest yields (Fig. S4). The difference in catalytic activities is reasonably assigned to homogeneous-like feature of PDVB-VP-*n* in the solvent of cyclohexane where each of pyridine groups is completely exposed to the reactants. Additionally, PVP in the solvent of cyclohexane also gives low conversion (33.2%) due to its poor dissolution. When PVP dissolved in ethanol as a homogeneous catalyst, the yield of 97% is obtained, which is similar to the value of PDVB-VP-20 (96%). These results confirm that PDVB-VP-20 is a homogeneous-like base catalyst. Fig. 5c shows catalytic yields of reusable PDVB-VP-20 catalyst in the substrate of benzaldehyde. After recycling for 5 times, the conversion of benzaldehyde is still higher than 96%, indicating its superior stability. N_2 isotherm of PDVB-VP-20 recycled for 5 times shows similar textural parameters to fresh PDVB-VP-20, indicating its excellent stability of porous structure during reactions (Table 1, Fig. S5). Furthermore, various substrates aromatic, aliphatic and heteroatamatic aldehydes have been used to react with malononitrile over PDVB-VP-20 catalyst (Fig. 5d and Table 2). All substrates exhibit high conversions to the corresponding products. For example, cyclohexanone and furfural give the yields of 92.6 and 95.1%, respectively.

4. Conclusions

In summary, we have demonstrated a preparation of swelling porous polymers with pyridine groups. These novel polymers are designed as homogeneous-like base catalysts, which exhibit outstanding catalytic activities and long catalyst life in the Knoevenagel condensation of malononitrile and various aldehydes. The development of homogeneous-like solid catalysts might bring out a new concept for designing efficient heterogeneous catalysts.

Acknowledgments

This work was supported by theState Basic Research Project of China (2009CB623507), Sinopec, and the National Natural Science Foundation of China (20773049). We also acknowledge the financial support from NSFC under grant nos. 61008014.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.04.020.

References

[1] D.S. Su, ChemSusChem 2 (2009) 1009–1020.
[2] V.I. Parvulescu, C. Hardacre, Chem. Rev. 107 (2007) 2615–2665.
[3] D.J. Gorin, B.D. Sherry, F.D. Toste, Chem. Rev. 108 (2008) 3351–3378.
[4] D.E. Bergbreiter, J.H. Tian, C. Hongfa, Chem. Rev. 109 (2009) 530–582.
[5] B. Cornils, W.A. Herrmann, J. Catal. 216 (2003) 23–31.
[6] D.S. Su, J. Zhang, B. Frank, A. Thomas, X.C. Wang, J. Paraknowitsch, R. Schlogl, ChemSusChem 3 (2010) 169–180.
[7] M. Tu, R.J. Davis, J. Catal. 199 (2001) 85–91.
[8] J.L. Hu, K.X. Li, W. Li, F.Y. Ma, Y.H. Guo, Appl. Catal. A Gen 364 (2009) 211–220.
[9] L.L. Xu, Y.H. Wang, X. Yang, X.D. Yu, Y.H. Guo, J.H. Clark, Green Chem. 10 (2008) 746–755.
[10] Z. Mu, J.J. Li, M.H. Duan, Z.P. Hao, S.Z. Qiao, Catal. Commun. 9 (2008) 1874–1877.
[11] C.Y. Ma, Z. Mu, J.J. Li, Y.G. Jin, J. Cheng, G.Q. Lu, Z.P. Hao, S.Z. Qiao, J. Am. Chem. Soc. 132 (2010) 2608–2613.
[12] T. Yokoi, M. Yoshioka, H. Ima, T. Tatsumi, Angew. Chem. Int. Ed. 48 (2009) 9884–9887.
[13] T. Yokoi, H. Yoshitake, T. Yamada, Y. Kubota, T. Tatsumi, J. Mater. Chem. 16 (2006) 1125–1135.
[14] T. Yokoi, H. Yoshitake, T. Tatsumi, J. Mater. Chem. 14 (2004) 951–957.
[15] Q.H. Yang, J. Liu, L. Zhang, C. Li, J. Mater. Chem. 19 (2009) 1945–1955.
[16] J. Liu, S.Z. Qiao, S.B. Hartono, G.Q. Lu, Angew. Chem. Int. Ed. 49 (2010) 4981–4985.
[17] P. Bai, P.P. Wu, G.F. Zhao, Z.F. Yan, X.S. Zhao, J. Mater. Chem. 18 (2008) 74–76.
[18] P.P. Wu, P. Bai, K.P. Loh, X.S. Zhao, Catal. Today 158 (2010) 220–227.
[19] X.Y. Yang, Y. Li, G. Van Tendeloo, F.S. Xiao, B.L. Su, Adv. Mater. 21 (2009) 1368–1372.
[20] J. Perez-Ramirez, C.H. Christensen, K. Egeblad, C.H. Christensen, J.C. Groen, Chem. Soc. Rev. 37 (2008) 2530–2542.
[21] F.S. Xiao, L.F. Wang, C.Y. Yin, K.F. Lin, Y. Di, J.X. Li, R.R. Xu, D.S. Su, R. Schlogl, T. Yokoi, T. Tatsumi, Angew. Chem. Int. Ed. 45 (2006) 3090–3093.
[22] Y. Leng, J. Wang, D.R. Zhu, X.Q. Ren, H.Q. Ge, L. Shen, Angew. Chem. Int. Ed. 48 (2009) 168–171.

[23] M.J. O'Donnell, Acc. Chem. Res. 37 (2004) 506–517.
[24] Y.L. Zhang, S. Wei, F.J. Liu, Y.C. Du, S. Liu, Y.Y. Ji, T. Yokoi, T. Tatsumi, F.S. Xiao, Nano Today 4 (2009) 135–142.
[25] U. Costantino, F. Marmottini, M. Nocchetti, R. Vivani, Eur. J. Inorg. Chem. 10 (1998) 1439–1446.
[26] A.J. Pardey, A.D. Rojas, J.E. Yanez, P. Betancourt, C. Scott, C. Chinea, C. Urbina, D. Moronta, C. Longo, Polyhedro 24 (2005) 511–519.
[27] M.P. McCurdie, L.A. Belfiore, Polymer 40 (1999) 2889–2902.
[28] X. Wang, K.S.K. Lin, J.C.C. Chan, S. Cheng, J. Phys. Chem. B 109 (2005) 1763–1769.
[29] Y. Xia, R. Mokaya, Angew. Chem. Int. Ed. 42 (2003) 2639–2644.
[30] R. Xing, H.H. Wu, X.H. Li, Z.L. Zhao, Y.M. Liu, L. Chen, P. Wu, J. Mater. Chem. 19 (2009) 4004–4011.