

Synthesis of Ionic Liquid Functionalized SBA-15 Mesoporous Materials as Heterogeneous Catalyst toward Knoevenagel Condensation under Solvent-Free Conditions

Yong Liu,^[a] Jiajian Peng,^[a] Shangru Zhai,^[b] Jiayun Li,^[a] Jianjiang Mao,^[a] Meijiang Li,^[a] Huayu Qiu,^{*[a]} and Guoqiao Lai^{*[a]}

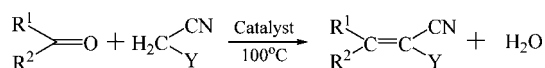
Keywords: Mesoporous materials / Heterogeneous catalysis / Ionic liquids

1-Methyl-3-propylimidazolium chloride (MPIImCl) and 1-propylpyridinium chloride (PPyCl) ionic liquid functionalized SBA-15 mesoporous materials were synthesized and used as heterogeneous catalysts in Knoevenagel reactions with excellent yields and reusability.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

The Knoevenagel condensation, one of the most important preparation methods of substituted alkenes, is widely employed to synthesize intermediates of fine chemicals (Scheme 1). Compared to traditional homogeneous catalysts including organic bases (primary, secondary, tertiary amines), ZnCl₂, LiCl, and cetyltrimethylammonium bromide (CTAB),^[1] solid-based heterogeneous catalysts are more desirable for their advantages in separation and reusability. In recent years, resins, zeolites, hydrotalcites etc. have been applied to this reaction as heterogeneous catalysts,^[2] among which organo-functionalized mesoporous silicas are specially studied due to their unique properties such as high surface area, uniform pore structure and controllable surface properties.^[3] Recently, synthesis and catalysis activities of different structured mesoporous materials functionalized by amino/diamino groups have been reported.^[4]



Scheme 1.

Ionic liquids, known as novel environmental benign media, have attracted great interest in the last two decades^[5] since they can serve not only as favorable solvents for catal-

ysis but also as green catalysts themselves in many reactions such as cycloaddition, Biginelli reaction, nitration, Beckmann rearrangement^[6] and Knoevenagel condensation as well.^[7] However, in some cases ionic liquids are miscible with some products or reactants, leaving separation and reuse of catalyst still a problem. Thus, immobilization of ionic liquids on solid-based materials is of particular interest. Recently, several groups reported the successful synthesis of silica-based ionic liquids,^[8] while reports on ordered ionic liquids functionalized mesoporous materials are still quite rare.^[9] Herein, we report the synthesis of MPIImCl and ionic liquid functionalized SBA-15 mesoporous material and its catalytic activity toward Knoevenagel condensation under solvent-free conditions. The resulting heterogeneous catalyst could be easily recovered with high catalytic activity remaining after 10 cycles.

Results and Discussion

1-Methyl-3-[(triethoxysilyl)propyl]imidazolium chloride (MTESPIImCl) and 1-[(triethoxysilyl)propyl]pyridinium chloride (TESPPyCl) were prepared by the reaction of 1-methylimidazole or pyridine with (3-chloropropyl)triethoxysilane, different from the literature^[8a] not only because the reactants were cheaper but also the corresponding pyridine species could be obtained. The XRD patterns of the MPIImCl-SBA materials obtained with different MTESPIImCl amounts are given in Figure 1. When the MTESPIImCl content in the initial mixture was 5%, one intense diffraction peak together with two weak ones could be seen (Figure 1, b), corresponding to the (100), (110), and (200) planes of highly ordered SBA-15 structured mesoporous materials, respectively. As the MTESPIImCl content increased to 10%, the (110) and (200) peaks disappeared (Fig-

[a] Key Laboratory of Organosilicon Chemistry and Material Technology of the Ministry of Education, Hangzhou Teachers College, Hangzhou 310012, China
Fax: +86-571-28865135
E-mail: yjg@hztc.edu.cn

[b] Department of Chemical Engineering and Materials, Dalian Institute of Light Industry, Dalian 116034, China

ure 1, c), indicating the decrease of pore regularity. With a further increase of the MTESPIImCl content to 15%, no characteristic peaks of SBA-15 mesoporous materials could be seen. It is noteworthy that when the pre-hydrolysis time of tetraethyl orthosilicate (TEOS) was prolonged to 4 h, the order of pore structure (MTESPIImCl content 10%) was greatly improved (Figure 1, a). Similar phenomena have been reported in the synthesis of sulfonic acid and aminopropyl functionalized SBA-15 mesoporous materials under acid conditions^[4c,10] and could be explained by the following reasons: On one hand, MTESPIImCl can perturb the self-assembly of surfactant micelles and silica precursors; on the other hand, the cationic part of MTESPIImCl probably interacts with ethoxy groups of TEOS, thus inhibiting its hydrolysis and condensation. Therefore, prolonging the pre-hydrolysis time of TEOS can prevent MTESPIImCl from disturbing the mesophase. XRD results of PPy-SBA materials also proved that ordered structures could be obtained with TEOS pre-hydrolyzed for 4 h (Figure 2).

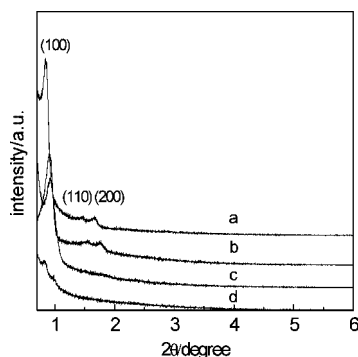


Figure 1. XRD patterns of MPIImCl-SBA materials with different MTESPIImCl contents and different TEOS pre-hydrolyze times.

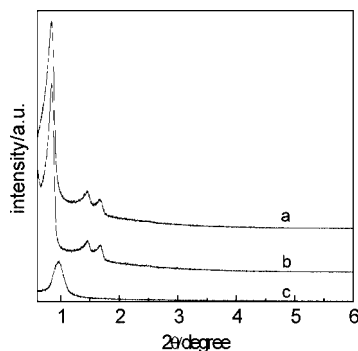


Figure 2. XRD patterns of PPyCl-SBA materials with different TESPPyCl contents with TEOS prehydrolyzed for 4 h; a: 5%, b: 10%, c: 15%.

N₂ adsorption-desorption was carried out to supply further information about the physical properties of the ionic liquid functionalized SBA-15 materials. As shown in Table 1, surface areas, pore volumes and pore diameters of the products all decreased as the ionic liquid content increased from 0 to 15%, which could be attributed to the increasing distribution of ionic liquid moieties in the interior mesopore surfaces. PPy-SBA materials were found to

display higher surface areas and larger pore diameters compared with MPIImCl counterparts, and longer pre-hydrolysis time was found helpful to improve the structures of products, which was in agreement with XRD results. Elemental analysis was used to obtain accurate amounts of the ionic liquid attached to the mesopores. As summarized in Table 1, loading amounts of PPy-SBA and MPIImCl-SBA were comparable and increased with the increase of the ionic liquid contents in the initial mixture. The effect of pre-hydrolysis time on the loading amounts was negligible. Solid-state ²⁹Si NMR spectroscopy and thermogravimetric analysis (TGA) were also used to characterize the ionic liquid functionalized mesoporous materials and the results well agree with that of the elemental analysis.

Table 1. N₂ adsorption-desorption and elemental analysis results of ionic liquid functionalized SBA-15 materials.

Ionic liquid, amount [%]	<i>S</i> _{BET} [m ² /g]	<i>V</i> _p [cm ³ /g]	Pore diameter [nm]	Loading amount [mmol/g]
–, 0 ^[a]	688	0.937	5.51	0
MTESPIImCl, 5 ^[a]	482	0.849	5.33	0.512
MTESPIImCl, 10 ^[a]	400	0.564	5.13	0.943
MTESPIImCl, 15 ^[a]	143	0.221	4.12	1.322
MTESPIImCl, 10 ^[b]	529	0.653	5.89	0.966
TESPPyCl, 5 ^[b]	558	0.997	8.04	0.569
TESPPyCl, 10 ^[b]	504	0.901	8.03	0.986
TESPPyCl, 15 ^[b]	368	0.775	5.74	1.409

[a] TEOS pre-hydrolysis time 40 min. [b] TEOS pre-hydrolysis time 4 h.

In view of the increasing emphasis on the adoption of clean manufacturing processes and environmentally benign technologies, clean, solvent-free and highly efficient catalytic technologies for the chemical production are highly desirable, so we carried out the Koevenagel condensation of various aldehydes with malononitrile/ethyl cyanoacetate at 100 °C under solvent-free conditions. 10% MPIImCl-SBA and 10% PPy-SBA were used as catalysts, respectively, and the optimal amount of catalyst was determined to be 0.8 mol-% based on the reaction of benzaldehyde with malononitrile (Table 2, Entries 1–3). As illustrated in Table 2 (Entries 4, 6, 13, 15), the catalytic activities of PPy-SBA were slightly lower than those of MPIImCl-SBA; thus, MPIImCl-SBA was selected as catalyst for the other reactions. As shown in Entries 7–10, reactions of malononitrile with all tested aldehydes were complete in 3.5 h with excellent yields (not lower than 87%), which was not lower (if not higher) compared with those in traditional homogeneous systems.^[1,2] The influence of substituents in the aromatic ring was negligible, indicating the high catalysis activity of the MPIImCl-SBA materials. In the case of ethyl cyanoacetate, however, the yields decreased even if the reaction time was prolonged to 6 h (Entries 9–15). Besides, aldehydes with electron-donating groups (Entries 11, 14, 15) showed lower yields compared with the others. The reusability of the MPIImCl-SBA materials was examined by the reaction of benzaldehyde with malononitrile. As shown in Entry 20, a yield as high as 86.1% was obtained in the 10th cycle.

Table 2. Knoevenagel condensation of aldehydes with malononitrile/ethyl cyanoacetate.

Entry	R ¹	R ²	Y	Ionic liquid amount [mol-%]	Time [h]	Isolated yield [%]
1	Ph ^[a]	H	CN	0.2	3.5	63.5
2	Ph ^[a]	H	CN	0.4	3.5	89.6
3	Ph ^[a]	H	CN	0.8	3.5	93.5
4	Ph ^[b]	H	CN	0.8	3.5	92.8
5	2-ClC ₆ H ₄ ^[a]	H	CN	0.8	3.5	92.4
6	2-ClC ₆ H ₄ ^[b]	H	CN	0.8	3.5	89.6
7	4-MeOC ₆ H ₄ ^[a]	H	CN	0.8	3.5	89.6
8	4-ClC ₆ H ₄ ^[a]	H	CN	0.8	3.5	91.5
9	4-HOC ₆ H ₄ ^[a]	H	CN	0.8	3.5	87.7
10	4-MeC ₆ H ₄ ^[a]	H	CN	0.8	3.5	93.2
11	Ph ^[a]	H	CO ₂ Et	0.8	3.5	69.6
12	Ph ^[a]	H	CO ₂ Et	0.8	6.0	85.6
13	Ph ^[b]	H	CO ₂ Et	0.8	6.0	84.0
14	2-ClC ₆ H ₄ ^[a]	H	CO ₂ Et	0.8	6.0	90.5
15	2-ClC ₆ H ₄ ^[b]	H	CO ₂ Et	0.8	6.0	82.9
16	4-MeOC ₆ H ₄ ^[a]	H	CO ₂ Et	0.8	6.0	79.1
17	4-ClC ₆ H ₄ ^[a]	H	CO ₂ Et	0.8	6.0	86.9
18	4-HOC ₆ H ₄ ^[a]	H	CO ₂ Et	0.8	6.0	81.4
19	4-MeC ₆ H ₄ ^[a]	H	CO ₂ Et	0.8	6.0	75.0
20	Ph ^[a,c]	H	CN	0.8	3.5	86.1

[a] MPlmCl-SBA as catalyst. [b] PpyCl-SBA as catalyst. [c] MPlmCl-SBA in the 10th cycle.

In summary, ionic liquid functionalized SBA-15 mesoporous materials were synthesized and gave high yields and good reusability in Knoevenagel condensations. These materials might be used not only as heterogeneous catalysts in reactions such as cycloaddition and Biginelli reactions but also as support for transition metals (work in this direction is in progress and will be reported soon).

Experimental Section

In a typical procedure to synthesize MPlmCl-SBA materials, 4.378 g of P123 (EO₂₀PO₇₀EO₂₀) was dissolved in 115 g of H₂O to which 25 g of HCl was added. After 10.17 mL (0.045 mol) of TEOS was added and pre-hydrolyzed for 40 min, 1.535 g (0.005) of MTE-SPlmCl was added. The mixture was stirred at 40 °C for 24 h and then transferred into a Teflon-lined stainless steel autoclave and kept at 100 °C for 24 h. The precipitate was filtered, subsequently washed with distilled water and EtOH, and dried at 60 °C in air. The template was removed by refluxing the as-synthesized material in EtOH for 24 h. The Knoevenagel condensation was carried out at 100 °C under solvent-free conditions. In a typical procedure, 1.82 g (0.025 mol) of malononitrile, 2.41 g (0.023 mol) of benzaldehyde and 0.22 g (0.2 mmol MPlmCl) of 10% MPlmCl-SBA were mixed and allowed to react for an appropriate time. The products were purified by column chromatography and the catalyst was filtered, washed with CH₂Cl₂, and collected for reusability test.

X-ray powder diffraction (XRD) data were acquired with a Rigaku D/max 2500V/PC diffractometer with Cu-K_α radiation. N₂ adsorption and desorption isotherms were measured with a Quantacrome Autosorb-1 system at 77 K. Surface areas were calculated according to the BET method with relative pressures in the range 0.2–0.3, and pore volumes were taken at the $P/P_0 = 0.9923$ single point. Pore diameters were determined from absorption branches according to the Barrett–Joyner–Halenda (BJH) method. Loading amounts of ionic liquids were calculated from the nitrogen contents performed with an Elementar Vario EC III CHNOS element analyzer.

- a) G. Jones, *Org. React.* **1967**, *15*, 204–599; b) R. P. Shanthan, R. V. Venkataratnam, *Tetrahedron Lett.* **1991**, *32*, 5821–5823; c) G. Gowravaram, B. V. S. Reddy, R. S. Babu, J. S. Yadav, *Chem. Lett.* **1998**, 773–774; d) S. Wang, Z. Ren, W. Cao, W. Tong, *Synth. Commun.* **2001**, *31*, 673.
- a) Y. Goa, P. Wu, T. Tatsumi, *J. Catal.* **2004**, *224*, 107–114; b) J. Simpson, D. L. Rathbone, D. C. Billington, *Tetrahedron Lett.* **1999**, *40*, 7031–7033; c) F. A. Khan, J. Dash, R. Satapathy, S. K. Upadhyay, *Tetrahedron Lett.* **2004**, *45*, 3055–3058; d) M. L. Kantam, B. M. Choudary, C. K. Venkat Reddy, K. K. Rao, F. Figueras, *Chem. Commun.* **1998**, 1033–1034.
- a) A. Corma, *Chem. Rev.* **1997**, *97*, 2373–2419; b) A. Sayari, S. Hamoudi, *Chem. Mater.* **2001**, *13*, 3151–3168; c) C. Li, *Catal. Rev.* **2004**, *46*, 419–492; d) R. Corriu, A. Mehdi, C. Reye, *J. Organomet. Chem.* **2004**, *689*, 4437–4450.
- a) S. G. Wang, *Catal. Commun.* **2003**, *4*, 469–470; b) Y. Kubota, Y. Nishizaki, H. Ikeya, M. Saeki, T. Hida, S. Kawazu, M. Yoshida, H. Fujii, Y. Sugi, *Microporous Mesoporous Mater.* **2004**, *70*, 135–149; c) X. G. Wang, K. S. K. Lin, J. C. C. Chan, S. Cheng, *J. Phys. Chem. B* **2005**, *109*, 1763–1769; d) D. Brunel, *Microporous Mesoporous Mater.* **1999**, *27*, 329–344.
- a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2083; b) J. Dupont, R. F. Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667–3692; c) A. Ouadi, B. Gadenne, P. Hesemann, J. J. E. Moreau, I. Billard, C. Gaillard, S. Mekki, G. Moutiers, *Chem. Eur. J.* **2006**, *12*, 3074–3081; d) M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, *Angew. Chem. Int. Ed.* **2004**, *43*, 4988–4992; e) J. Dupont, *J. Braz. Chem. Soc.* **2004**, *15*, 341–350.
- a) J. J. Peng, Y. Q. Deng, *New J. Chem.* **2001**, *25*, 639–641; b) J. M. Sun, S. I. Fujita, M. Arai, *J. Organomet. Chem.* **2005**, *690*, 3490–3497; c) J. J. Peng, Y. Q. Deng, *Tetrahedron Lett.* **2001**, *42*, 5917–5919; d) K. Qiao, C. Yokoyama, *Chem. Lett.* **2004**, *33*, 808–809; e) J. J. Peng, Y. Q. Deng, *Tetrahedron Lett.* **2001**, *42*, 403–405.
- a) J. R. Harjani, S. J. Nara, M. M. Salunkhe, *Tetrahedron Lett.* **2002**, *43*, 1127–1130; b) D. C. Forbe, A. M. Law, D. W. Morrison, *Tetrahedron Lett.* **2006**, *47*, 1669–1703; c) P. Formentin, H. Garcia, A. Leyva, *J. Mol. Catal. A* **2004**, *214*, 137–142.
- a) C. P. Mehnert, R. A. Cook, N. C. Dispenziere, M. Afeworki, *J. Am. Chem. Soc.* **2002**, *124*, 12932–12933; b) C. P. Mehnert, E. J. Mozeleski, R. A. Cook, *Chem. Commun.* **2002**, 3010–3011; c) K. Qiao, H. Hagiwara, C. Yokoyama, *J. Mol. Catal. A* **2006**, *246*, 65–69.
- a) B. Gadenne, P. Hesemann, J. J. E. Moreau, *Chem. Commun.* **2004**, 1768–1769; b) M. H. Valkenberg, C. Castro, W. F. Hölderich, *Green Chem.* **2002**, *4*, 88–93.
- D. Margoless, J. A. Melero, S. C. Christiansen, B. F. Chmelka, G. D. Stucky, *Chem. Mater.* **2000**, *12*, 2448–2459.

Received: April 1, 2006
Published Online: June 12, 2006