Novel Periodic Mesoporous Silica Chlorides (PMSCl) with 2D P_6mm Hexagonal Structures: Efficient Catalysts for the Beckmann Rearrangement

Babak Karimi,* Hesam Behzadnia

Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Gava Zang, Zanjan 45137-6731, Iran Fax +98(241)4153232; E-mail: karimi@iasbs.ac.ir

Received 12 May 2010

Abstract: A family of ordered mesoporous silica chloride (SBA-Cl) with 2D $P_{o}mm$ hexagonal structures and high surface areas was prepared through treatment of SBA-15 with thionyl chloride. The materials were shown to have excellent catalytic activity in Beckmann rearrangements of ketoximes. The catalyst (SBA-Cl-2) was recovered and reused for at least three reaction cycles without significant change in its nanostructure as evidenced by surface analysis.

Key words: Beckmann rearrangement, silica chloride, ketoximes, amides, heterogeneous catalysis

Since the first reports on surfactant-templated mesoporous materials appeared in the past decade,¹ a wide variety of these materials, which possess uniform channels with large pore size (2-40 nm), high surface area (up to 2000 m^2 g⁻¹), and tuneable structure have been synthesized.² Furthermore, organically functionalized ordered mesoporous silicas³ with tailored composition has also been widely investigated for applications in adsorbent synthesis,⁴ gas separation techniques,5 photocontrollable molecular storage,⁶ catalysis,⁷ molecular recognition,⁸ nanoreactors,⁹ and biological uses.¹⁰ The surface properties of mesoporous silicates can be easily modified with different chemical groups, by which their functionality and textural properties could be changed. In earlier studies, these chemical groups were incorporated into ordered mesoporous silicas through direct co-condensation or post-grafting of trialkoxysilane R1Si(OR2)3 which resulted in terminally bonded organic groups inside the channels.^{7,11} Another less frequently used method was direct chlorination of surface Si–OH groups to generate Si–Cl functions as precursors for grafting of the organic moiety onto silica surfaces.^{7,11} In this approach organic groups were bound robustly, and owing to higher stability of Si-C bond between the organic moiety and the surface, they were typically less prone to leaching than those attached via conventional grafting. Furthermore, many potential applications that exploited high surface activities of these chlorinated silicas were demonstrated in catalysis,¹² water softening,¹³ chromatography,¹⁴ and functional-group interconversions.¹⁵ However, most of these amorphous silica chlorides often had low surface areas (up to $100 \text{ m}^2 \text{ g}^{-1}$), large distributions in pore diameters and void volumes. They also suffer from the disadvantage of low surface

rides have already been prepared from the corresponding amorphous silica, to the best of our knowledge, there is no report about the same transformation with the use of ordered mesoporous silicas. If such a transformation could be attained without significant change in structural features of the parent ordered silica, it would be possible to prepare a variety of sophisticated ordered mesoporous chlorosilicates with attractive properties including high surface area, high surface Si-Cl loading, and large ordered pores with narrow size distributions. Here, we have chosen to employ mesoporous silica SBA-15² as the precursor for preparation of chlorinated silica, not only because it has larger and more accessible channels but also because it displays higher thermal and hydrothermal stability than M41S family.1 SBA-15 was obtained from pluronic P123 and (EtO)₄Si under acidic conditions according to the reported procedure.² The surfactant-free SBA-15 was obtained by subsequent removal of pluronic P123 through extensive extraction with ethanol for 48 hours. The resulting SBA-15 was then separately allowed to react with excess of thionyl chloride under reflux conditions for 24 and 48 hours, to afford the corresponding surface chlorinated SBA-Cl-1, SBA-Cl-2, respectively. The excess of thionyl chloride was distilled off and the resulting product was calcined at ca. 550 °C and stored in a sealed vessel, under dry argon atmosphere. The materials were characterized by simultaneous thermal analysis, surface analysis, and transmission electron microscopy.

chlorine contents. While several types of solid silica chlo-

Table 1 Characterization of Materials

| Entry | Compd | $\mathbf{S}_{\text{BET}}^{\ a}$ | Pore Size ^b | V_P^c | Cl content ^d |
|-------|-----------------------|---------------------------------|------------------------|---------|-------------------------|
| 1 | SBA-15 | 870 | 6.3 | 0.87 | - |
| 2 | SBA-Cl-1 | 710 | 5.1 | 0.80 | 1.7 |
| 3 | SBA-Cl-2 | 682 | 5.3 | 0.79 | 3.4 |
| 4 | recovered SBA-Cl-2 | 363 | 7.9 | 0.72 | 2.8 |
| 5 | silica-Cl | 408 | 5.98 | 0.61 | 2.2 |

^a BET surface area (m² g⁻¹).

^b BJH average pore diameter (nm).

^c Total pore volume (cm³ g⁻¹).

^d Surface Si–Cl content (mmol g⁻¹) determined by back titration using (0.01 M NaOH) after hydrolysis and elemental analysis.

SYNLETT 2010, No. 13, pp 2019–2023

Advanced online publication: 09.07.2010

DOI: 10.1055/s-0030-1258484; Art ID: Y01310ST

© Georg Thieme Verlag Stuttgart · New York



Figure 1 Nitrogen adsorption–desorption isotherms for mesoporous A) SBA-15, B) SBA-Cl-1, C) SBA-Cl-2, and D) recovered SBA-Cl-2. Inset: BJH pore size distributions obtained from the corresponding isotherms.

Nitrogen adsorption-desorption of two samples provided very clear type IV profiles with sharp hysteresis loop, which is characteristic of the highly ordered mesoporous materials (Figure 1). Interestingly, the capillary condensation step (observed at relative pressure between 0.6–0.8) was clearly remained even after calcination of the samples at ca. 550 °C, which provided clear evidence for the preservation of ordered mesopore structures in both SBA-Cl-1 and SBA-Cl-2.

It is also noteworthy that even after surface chlorination followed by calcination at ca. 550 °C, the resulting surface chlorinated materials exhibited a specific surface area of ca. 710 $m^2 g^{-1}$ and 682 $m^2 g^{-1}$ and total pore volumes of 0.8 and 0.79 cm³ g⁻¹, respectively (Table 1, entry 2 and 3). BJH calculation showed an average pore diameter of 6.3 nm for the starting SBA-15 (Table 1, entry 1), 5.1 nm for SBA-Cl-1, and 5.3 nm for SBA-Cl-2 (Table 1, entry 1-3), which were in good agreement with pore diameters estimated from TEM images (Figure 2). Moreover, the TEM images of all chlorinated samples showed ordered domains that appeared to have a two-dimensional hexagonal (P_6mm) symmetry similar to the parent SBA-15 materials. The accurate images also provided further evidence that the ordered phase dominated any disordered (amorphous) silicate phases in all of the samples that were investigated.



Figure 2 TEM images of (A, B) SBA-Cl-1; (C, D) SBA-Cl-2

Synlett 2010, No. 13, 2019–2023 © Thieme Stuttgart · New York

As it clearly could be seen from BJH average pore-size calculations, the pore diameters decreased by up to 1 nm, when the parent SBA-15 was chlorinated under the described chlorination protocol.

The BJH calculations also indicated a narrow pore-size distributions for both SBA-Cl-1 and SBA-Cl-2 in the mesoporous region (Figure 1, B and C). These distributions interestingly showed that the nanoarchitecture of the samples (ordered mesoporous channels) largely survived even after prolonged reflux in excess thionyl chloride during the preparation stage and also after calcinatation at 550 °C.

The chlorine contents of the materials were also determined with the use of back-titration of the resulting HCl upon the treatment of the materials with deionized water for 12 hours. These values were further corroborated with elemental analysis to be 1.7 and 3.4 mmol g⁻¹ for SBA-Cl-1 and SBA-Cl-2, respectively. All samples were preheated at 550 °C under dry argon atmosphere, before performing hydrolysis and titration experiments. These results clearly excluded any interference that might be resulted from physically adsorbed HCl in the calculation of total chlorine content. Consequently the observed data for chlorine content could be truly related to Si-Cl moieties throughout the structure. It is also worth mentioning that these materials, regardless to their Cl content, were highly stable upon storage for months under an inert atmosphere. Encouraged by high surface area, high chlorine content of the surface, and highly stable and ordered structures of SBA-Cl, we speculated whether these materials might also be suitable catalysts (or reagents) in some organic tranformations. Along the line of this hypothesis, we were also interested to study the catalytic performance of SBA-Cl in the Beckmann rearrangement. The Beckmann rearrangment is a common organic transformation to convert ketoxime into amides.16 One of the most important industrial version of this reaction is the rearrangement of cyclohexanone oxime with oleum to ε -caprolactam sulfate that is a precursor for production of Nylon-6.¹⁷ However, this method is accompanied by the co-production of million tons of undesired ammonium sulfate and also suffers from serious corrosion problems during liquid-phase industrial processes. As a result, several efforts have been directed toward the development of milder methods for Beckmann rearrangement by using catalysts that replace the more traditional and stoichiometric ones.¹⁸ However, most of these protocols need expensive reagents, or suffer from the tedious workup procedures. If this rearrangement could be performed by the use of solid catalysts, because of the ease with which the catalyst could be separated from product and recycled, the reaction would be considerably cheaper and environmentally more friendly. Along this line, several catalysts have been investigated and include silica-supported molybdenum(VI) oxide,¹⁹ silica sulfate,²⁰ solid sulfonic acid resin,²¹ Al-MCM-41 molecular sieves,²² zeolites,^{23,24a-h} MCM-22,²⁴ⁱ silicoalumino phosphates^{24j} and titano silicate.^{24k} While these methods have provided considerable improvement in the Beckmann rearrangement, they often require high temperature (over 130 °C), high catalyst loading, high concentrations of strongly acidic additives and/or special apparatus for vapor-phase Beckmann rearrangements. It is also noted that the chemical yields and selectivities of the corresponding products are not always satisfactory. Therefore, it seems that there is still much room to develop new methods for heterogeneous and catalytic Beckmann rearrangements under mild and more appropriate reaction conditions. As summarized in Table 2, we found that SBA-Cl-2 is an efficient catalyst for the Beckmann rearrangement of a large number of ketoximes. Different solvents were investigated for this transformation and it turned out that refluxing toluene could led to higher yields of products. Most of the products were easily separated in almost pure form with a simple filtration of catalyst and evaporation of the solvent under reduced pressure.

The catalyst (SBA-Cl-2) was recovered in the Beckmann rearrangement of acetophenone oxime by simple separation and was used directly for the next round of reaction (Table 2, entries 5 and 6). Interestingly, the nanostructure of the catalyst remained unchanged after the third reaction recycle, although, a significant change in the surface area (from 682 to 383 $m^2 g^{-1}$) and a slight decrease in the total pore volume from 0.79 to 0.72 cm³ g⁻¹ and chlorine content (from 3.4 to 2.8 mmol g^{-1}) occurred (Table 1, Figure 1, D). These results clearly showed that the catalyst was highly stable and no significant restructuring of the catalyst took place on multiple uses. Interestingly, we observed that the stored sample showed essentially the same reactivity as that of the fresh catalyst. This observation definitively proved that ordered mesoporous silica chlorides were indeed stable at room temperature under an inert asmosphere. It was very important to note that upon the use of amorphous silica chloride (SiO₂Cl)¹² under the same reaction conditions, the corresponding products were obtained in very low yields (Table 2, entry 3). This result clearly showed that the SBA-Cl was a much more active catalyst in comparison with the amorphous silica chloride in the model reaction. Particularly, SBA-Cl-2 also showed excellent activity in the selective Beckmann rearrangement of cyclohexanone oxime to ε -caprolactam, without the formation of any byproducts (Table 2, entry 15).

 Table 2
 Beckmann Rearrangement of Various Oximes Using

 SBA-CI-2
 Particular State

Efficient Catalysts for the Beckmann Rearrangement

| HO | R^2 R^1 R^1 | BA-Cl- tolue | -2 (20 mol%) ne, reflux | R ¹ H | R ² |
|-------|---------------------------------------|-----------------------------|------------------------------------|-------------------------|--------------------------|
| Entry | \mathbb{R}^1 | | R ² | Time (h) | Yield (%) ^{a,b} |
| 1 | Ph | | Ph | 2.5 | 100 |
| 2 | Ph | | Ph | 2.5 | 98° |
| 3 | Ph | | Ph | 5 | 7^{d} |
| 4 | Ph | | Me | 3 | 100 |
| 5 | Ph | | Me | 3 | 92 ^e |
| 6 | Ph | | Me | 3 | 83 ^f |
| 7 | 4-MeOC ₆ H ₄ | | Me | 10 | 95 |
| 8 | 3-MeOC ₆ H ₄ | | Me | 12 | 68 |
| 9 | 4-MeOC ₆ H ₄ | | 4-MeOC ₆ H ₄ | 5 | 82 |
| 10 | 2-MeOC ₆ H ₄ | | Me | 2 | 100 |
| 11 | 4-MeC ₆ H ₄ | | Me | 3 | 95 |
| 12 | 3,4-(MeO) ₂ C ₆ | ₅ H ₃ | Me | 12 | 89 |
| 13 | Ph | | Et | 8 | 92 |
| 14 | $4-PhC_6H_4$ | | Me | 8 | 60 |
| 15 | HO N | \rangle | | 35 | 88 |

^a All the products are known.²⁵

^b Isolated yield.

^c Reaction was carried out using a three months stored sample of SBA-Cl-2 under an inert atmosphere.

^d Reaction using amorphous silica chloride.

^e Second run.

^f Third run.

The precise mechanism for this reaction is unclear at this stage. However, it seems reasonable that SBA-Cl-2 might act as a Lewis acid (through its surface Si-Cl bonds) since it has calcined at 550 °C in order to minimize the contribution of physically adsobed HCl. Therefore, a plausible idea is that SBA-Cl-2 reacts with oxime to produce the corresponding O-silvlated oxime 1 and HCl. The resulted HCl is then captured by the rearranged intermediate 2 to afford the Beckmann products and concomitant release of SBA-Cl-2 that in turn re-enter to the catalytic cycle (Scheme 1). Nevertheless, it is difficult at this stage to exactly attribute the actual catalytic activity to solely surface Si-Cl bonds. Based on the moisture-sensitive nature of SBA-Cl-2, it would not be also surprise if this material serves as a source for in situ formation of a trace HCl. Further studies on this particular subject are currently under way to clarify this issue, and the results will be appearing in due course.



Scheme 1 Proposed mechanism for the Beckmann reaction using SBA-Cl-2

In conclusion we described a novel route for the synthesis of a family of ordered mesoporous chlorinated silica (namely SBA-Cl-1 and SBA-Cl-2) with 2D P_6mm hexagonal structures and tunable wt% of chlorine by treating SBA-15 with thionyl chloride. We also demonstrated that these materials are effective catalysts for the Beckmann rearrangements of various types of ketoximes. Owing to high surface area, high mesopores volume, and tunable wt% of chlorine content, these nano silica chlorides could be considered as very promising materials in catalysis, and also in the preparation of new highly loaded stationary phase for various types of chromatographic techniques. Study on further applications of these materials and the mechanistic feature of the reaction are currently ongoing in our laboratory.

General Procedure for the Beckmann Rearrangement Using SBA-Cl-2

In a 10 mL glass flask equipped with a magnetic stirrer and condenser, we placed oxime (1 mmol) and SBA-Cl (20 mol%) in toluene (3 mL). The mixture was refluxed in appropriate time. The reaction was monitored by TLC, and after completion of the reaction, most of products were easily extracted with a simple filtration of catalyst and evaporation of the solvent under reduced pressure. In other cases the crude products were required to purification on silica gel using a mixture of *n*-hexane and EtOAc to give the isolated products in yields stated in Table 2. Noteworthy, when the reaction was performed using large scale of acetophenone oxime (10 mmol, 1.35 g) the corresponding amide was obtained in 92% yield (1.24 g) under similar reaction conditions.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

Acknowledgment

The authors acknowledge IASBS and INSF Research Councils for support of this work. We also acknowledge Dr. Saeed Emadi for correcting the manuscript.

Synlett 2010, No. 13, 2019–2023 © Thieme Stuttgart · New York

References

- (1) (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature (London)* **1992**, *359*, 710.
 (b) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
- (2) (a) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* 1998, 279, 548. (b) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* 1998, *120*, 6024.
- (3) (a) Davis, M. E. *Nature (London)* 2002, *417*, 813. (b) Stein, A. *Adv. Mater.* 2003, *15*, 763. (c) Hoffmann, F.; Cornelius, M.; Morell, J.; Fröba, M. *Angew. Chem. Int. Ed.* 2006, *45*, 3216.
- (4) (a) Feng, X.; Fryxell, G. E.; Wang, L. Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997**, *276*, 923. (b) Mori, Y.; Pinnavaia, T. J. *Chem. Mater.* **2001**, *13*, 2173. (c) Mercier, L.; Pinnavaia, T. J. *Adv. Mater.* **1997**, *9*, 500. (d) Yoshitake, H. *New J. Chem.* **2005**, *29*, 1107.
- (5) Harlick, P. J. E.; Sayari, A. Ind. Eng. Chem. Res. 2007, 46, 446.
- (6) Mal, N. K.; Fujiwara, M.; Tanaka, Y. Nature (London) 2003, 421, 350.
- (7) (a) Wight, A. P.; Davis, M. E. Chem. Rev. 2002, 102, 3589.
 (b) Corma, A.; Garcia, H. Chem. Rev. 2002, 102, 3837.
 (c) Lu, Z. L.; Lindner, E.; Mayer, H. A. Chem. Rev. 2002, 102, 3543. (d) Mallat, T.; Baiker, A. Chem. Rev. 2004, 104, 3037. (e) Karimi, B.; Abedi, S.; Clark, J. H.; Budarin, V. Angew. Chem. Int. Ed. 2006, 45, 4776. (f) Karimi, B.; Biglari, A.; Clark, J. H.; Budarin, V. Angew. Chem. Int. Ed. 2006, 45, 4776. (g) Karimi, B.; Zamani, A.; Abedi, S.; Clark, J. H. Green Chem. 2009, 109.
- (8) For more recent leading references, see: (a) Slowing, I.; Trewyn, B. G.; Lin, V. S. Y. J. Am. Chem. Soc. 2006, 128, 14792. (b) Casasffls, R.; Anzar, E.; Marcos, M. D.; Martínez-Máňez, R.; Sancenón, F.; Soto, J.; Amorós, P. Angew. Chem. Int. Ed. 2006, 45, 6661. (c) Coll, C.; Martínez-Máňez, R.; Marcos, M. D.; Sancenón, F.; Soto, J. Angew. Chem. Int. Ed. 2007, 46, 1675.
- (9) (a) Zhang, R.; Ding, W.; Tu, B.; Zhao, D. Y. *Chem. Mater.* 2007, *19*, 4379. (b) Inumaru, K.; Ishihara, T.; Kamiya, Y.; Okuhara, T.; Yamanaka, S. *Angew. Chem. Int. Ed.* 2007, *46*, 7625. (c) Karimi, B.; Zareyee, D. *Org. Lett.* 2008, *10*, 3989. (d) Otani, W.; Kinbara, K.; Zhang, Q.; Ariga, K.; Aida, T. *Chem. Eur. J.* 2007, *13*, 1731. (e) Karimi, B.; Zareyee, D. *J. Mater. Chem.* 2009, *19*, 8665.
- (10) (a) Hartmann, M. *Chem. Mater.* 2005, *17*, 4577.
 (b) Hudson, S.; Cooney, J.; Magner, E. *Angew. Chem. Int. Ed.* 2008, *47*, 8582.
- (11) Clark, J. H.; Macquarrie, D. J. Chem. Commun. 1998, 853.
- (12) (a) Sathe, M.; Ghorpade, R.; Kaushik, M. P. *Chem. Lett.*2006, *35*, 1048. (b) Clark, J. H.; Tavener, S. J.; Barlow, S. J. *Chem. Commun.* 1996, 2429. (c) Kamitori, Y.; Hojo, M.; Masuda, R.; Kimura, T.; Yoshida, T. *J. Org. Chem.* 1986, *51*, 1427. (d) Firouzabadi, H.; Iranpoor, N.; Karimi, B.; Hazarkhani, H. *Synlett* 2000, 263. (e) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H.; Karimi, B. *J. Org. Chem.* 2002, *67*, 2572.
- (13) Zolfigol, M. A.; Madrakian, T.; Ghaemi, E.; Afkhami, A.; Azizian, S.; Afshar, S. *Green Chem.* **2002**, *4*, 611.
- (14) (a) Helobe, P. J. Chromatogr. 1982, 245, 229. (b) Hadady, K. K. J. Chromatogr. 1992, 589, 301.
- (15) Salehi, P.; Zolfigol, M. A.; Shiri, F.; Baghbanzadeh, M. *Curr. Org. Chem.* **2006**, *10*, 2171.

- (16) Smith, M. B.; March, J. Advanced Organic Chemistry, 5th ed.; John Wiley and Sons: New York, 2001, 1415; and references cited therein.
- (17) Bellussi, G.; Perego, C. CATTECH 2000, 4, 4.
- (18) (a) Hashimoto, M.; Obora, Y.; Sakaguchi, S.; Ishii, Y. J. Org. Chem. 2008, 73, 2894. (b) Hashimoto, M.; Obora, Y.; Ishii, Y. Org. Process Res. Dev. 2009, 13, 411.
 (c) Furuya, Y.; Ishihara, K.; Yamamoto, H. J. Am. Chem. Soc. 2005, 127, 11240. (d) De Luca, L.; Giacomelli, G.; Porcheddu, A. J. Org. Chem. 2002, 67, 6272. (e) Li, D.; Shi, F.; Guo, S.; Deng, Y. Tetrahedron Lett. 2005, 46, 671.
- (19) Dongare, M. K.; Bhagwat, V. V.; Ramana, C. V.; Gurjar, M. K. *Tetrahedron Lett.* **2004**, *45*, 4759.
- (20) Li, Z.; Ding, R.; Lu, Z.; Xiao, S.; Ma, X. J. Mol. Catal. A: Chem. 2006, 250, 100.
- (21) You, K.; Mao, L.; Yin, D.; Liu, P.; Luo, H. Catal. Commun. 2008, 9, 1521.
- (22) Ghiaci, M.; Aghaei, H.; Oroojeni, M.; Aghabarari, B.; Rives, V.; Vicente, M. A.; Sobrados, I.; Sanz, J. *Catal. Commun.* 2009, *10*, 1486.
- (23) Botella, P.; Corma, A.; Iborra, S.; Montón, R.; Rodríguez, I.; Costa, V. J. Catal. 2007, 250, 161.
- (24) (a) Heitmann, G. P.; Dahlhoff, G.; Hölderich, W. F. Appl. Catal., A 1999, 185, 99. (b) Li, W. C.; Lu, A. H.; Palkovits, R.; Schmidt, W.; Spliethoff, B.; Schüth, F. J. Am. Chem. Soc.
- 2005, 127, 12595. (c) Sirijaraensre, J.; Truong, T. N.; Limtrakul, J. J. Phys. Chem. B 2005, 109, 12099. (d) Marthala, V. R. R.; Jiang, Y.; Huang, J.; Wang, W.; Gläser, R.; Hunger, M. J. Am. Chem. Soc. 2006, 128, 14812. (e) Bonelli, B.; Forni, L.; Aloise, A.; Nagy, J. B.; Fornasari, G.; Garrone, E.; Gedeon, A.; Giordano, G.; Trifiro, F. Micropor. Mesopor. Mater. 2007, 101, 153. (f) Zhang, Y.; Wang, Y.; Bu, Y. Micropor. Mesopor. Mater. 2008, 107, 247. (g) Marthala, V. R. R.; Rabl, S.; Huang, J.; Rezai, S. A. S.; Thomas, B.; Hunger, M. J. Catal. 2008, 257, 134. (h) Palkovits, R.; Schmidt, W.; Ilhan, Y.; Erdem-Senatalar, A.; Schüth, F. Micropor. Mesopor. Mater. 2009, 117, 228. (i) Dahlhoff, G.; Barsnick, U.; Hölderich, W. F. Appl. Catal., A 2001, 210, 83. (j) Conesa, T. D.; Mokaya, R.; Yangb, Z.; Luque, R.; Campelo, J. M.; Romero, A. A. J. Catal. 2007, 252, 1. (k) Pavel, C. C.; Palkovits, R.; Schüth, F.; Schmidt, W. J. Catal. 2008, 254, 84.
- (25) (a) Furniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman: New York, **1978**, Chap. 7, 1116. (b) Furniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman: New York, **1978**, Chap. 8, 1222.

Copyright of Synlett is the property of Georg Thieme Verlag Stuttgart and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.