

ORIGINAL RESEARCH PAPER

Porous Acidic Catalyst, Functionalized with Imidazole Ionic Liquid ([SBA-Im]HSO₄) as a Novel Phase Transfer Catalyst for The Aqueous Synthesis of Benzyl Thiocyanates and Azides

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ABSTRACT

In the present study, application of porous acidic catalyst functionalized with an imidazole ionic liquid ([SBA-Im]HSO₄) as a phase transfer catalyst for the facile preparation of benzyl thiocyanates and azides in water has been described. The catalyst has been characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG). The polymeric phase transfer catalyst, easily recovered by simple filtration, shows no appreciable loss of activity when recycled several times.

Keywords: Phase transfer catalyst; Nucleophilic substitution; Porous catalyst; Benzyl halides.

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INTRODUCTION

Heterogenization of ionic liquids on solid is one of the important routes for developing novel supported ionic liquid (SIL) with the ability to maintain its activity and selectivity in catalysis. When we use homogeneous ILs, washing of the IL catalyst system for reusing and the separation of product from the ionic liquid needs large amounts of organic solvents [1]. The resulting material is solid and the ionic species dissolve in both water and organic solvent which can act as a suitable catalyst [2]. It has also been reported that supported ILs is more efficient than homogenous ionic liquids [1-4]. SILs offer exceptional opportunities to combine the important properties of ILs and heterogeneous catalysts and also to create entirely

new compositions with truly unique properties. Of interest has been to prepare hybrid materials where the ILs is bonded to a solid support skeleton framework [4].

In this regard, silica based materials appeared as a good catalyst supports, because of its easy availability and low cost [5,6]. The presence of hydroxy groups on the silica surface cause the rapid reaction of silica with alkoxy- or chlorosubstituted silyl compounds. This modification allows the introduction of heterogeneous catalysts and ILs to the surface of the support.

However, the wide-range pore distribution, irregular pore shape, low pore volume and low specific surface area of silica often lead to the low grafting amount of ILs and poor catalytic activities. To increase the grafting amount of ILs, the preparation and application of mesoporous

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materials for such applications have become an important method in heterogeneous catalysis.

Due to tunable pore sizes (5–30 nm), well-organized array of straight channel, high surface area, porosity structure, and also because of its thick pore walls, around 4 nm, which provide enhanced mechanical stability, SBA-15 has attracted a great deal of interest [7].

Mild synthesis condition of SBA-15 allowing for the immobilization of building blocks leads to a number of applications, such as gas storage, medicinal applications, adsorption, catalysis, pollutant removal, chromatography and sensor technology [8-12].

Recently, synthesis of efficient and recoverable phase-transfer catalysts attracts particular attention for reasons of economic and environmental impact. Phase-transfer catalysis (PTC) is an important tool technique, which is widely used for organic synthesis, particularly for nucleophilic substitution [13-16].

It is well known that the azide and thiocyanate compounds [17] play an important role as an intermediate in organic synthesis [18]. These compounds are generally carried out via nucleophilic substitution using thiocyanate and azide anions.

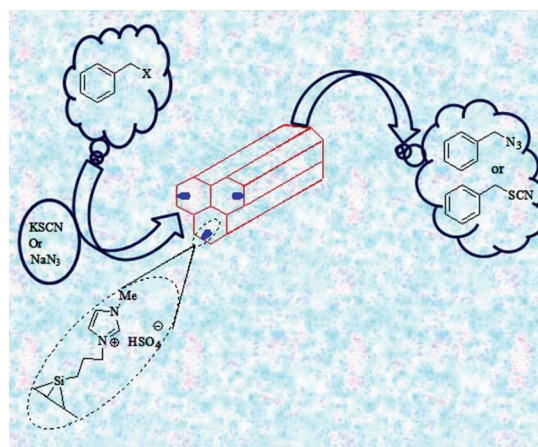
Even though some anticancer natural products, drug candidates, synthetic intermediates, antiasthmatic drugs, biocidal compounds and insecticides possess thiocyanate or azide functional groups, there are few reported practical synthetic routes in the literature for this class of compounds [19-21]. By having this goal in minds and in continuation of our research on using water as a reaction medium [22,23], in this research, we report the synthetic applicability of porous acidic catalyst functionalized with an imidazole ionic liquid ([SBA-Im]HSO₄) as a phase transfer catalyst for the facile preparation of benzyl thiocyanates and azides in water by nucleophilic substitution reaction (Scheme 1).

EXPERIMENTAL

General

Tetraethylorthosilicate (TEOS) and 3-chloropropyltriethoxysilane (CPTES) were used as silica sources and Pluronic P123 triblock copolymer (EO₂₀PO₇₀EO₂₀, MW 5800) was used as a structure-directing agent; all were supplied by Aldrich. Other chemical materials were purchased from Fluke and Merck companies

and used without further purification. The products were characterized by comparison of their physical data, IR and ¹H-NMR and ¹³CNMR spectra with known samples. NMR spectra were recorded on a Bruker Advance DPX 400 MHz instrument spectrometer using TMS as an internal standard. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrometer. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. The particle morphology was examined by SEM (Philips XL30 scanning electron microscope) and TEM (Zeiss-EM10C-80 kV). The TGA curve of the [SBA-Im]HSO₄ was recorded on a BHR, SPA 503 at heating rates of 10 °C min⁻¹ under air atmosphere, over the temperature range of 25-1000 °C.



Scheme. 1. Application of [SBA-Im]HSO₄ as a phase transfer catalyst for the facile preparation of benzyl thiocyanates and azides in water.

Synthesis of catalyst ([SBA-Im]HSO₄)

The viscous oil precursor 1-methyl-3-(3-(triethoxysilyl)propyl)imidazolium chloride ([Si-Im]Cl) was synthesized according to the reported method [24]. According to this method methyl imidazole (10 mmol) and an equimolar amount of (3-chloropropyl)triethoxysilane were heated under reflux at 95 °C for 30 h under a nitrogen atmosphere. Then, Mesoporous silica SBA-15 (3 g, previously dried overnight under vacuum at 180 °C) was prepared as reported elsewhere [25], and added to a solution of 1-methyl-3-(3-(triethoxysilyl)propyl)imidazolium chloride ([Si-Im]Cl; 6.0

mmol) in toluene (50 mL) and the mixture was heated under reflux for 24 h. After cooling to room temperature, the reaction mixture was filtered, and the resulting solid ([SBAIm]Cl) was washed with toluene and diethyl ether, followed by drying at 50 °C under reduced pressure. Finally, [SBA-Im]Cl (3.0 g) was suspended in dry CH_2Cl_2 (25 mL) in a three-necked, round-bottomed flask equipped with stirrer and ice bath. During vigorous stirring, concentrated H_2SO_4 (97 %) (6.0 mmol) was added drop by drop at 0 °C. The mixture was then warmed to room temperature, and heated under reflux for 48 h. The solid was isolated by filtration, washed with ethanol, then dried at room temperature.

Typical procedure for the conversion of benzyl halides to the corresponding benzyl thiocyanates and azides

To a magnetically stirred mixture of the benzyl halide (1.0 mmol) and nucleophilic reagents (KSCN or NaN_3) (1.5 mmol) in water (5 mL), [SBA-Im] HSO_4 (0.05 g, 0.049 mmol H^+) was added. The suspension was magnetically stirred at 90 °C for the lengths of time shown in Table 1. When the reaction did not proceed further, as indicated by TLC [using n-hexane/ethyl acetate (5:1)] and GC, the heterogeneous reaction mixture was filtered and the filtrate was extracted with diethyl ether (2×10 mL). The organic phase was dried over calcium chloride, filtered and then evaporated in vacuum to give the products in 83-92% isolated yields. After purification by column chromatography, the compounds were characterized on the basis of spectroscopic data (IR, ^1H & ^{13}C NMR) and by comparison with those reported in the literature.

pH-analysis of [SBAIm]HSO₄

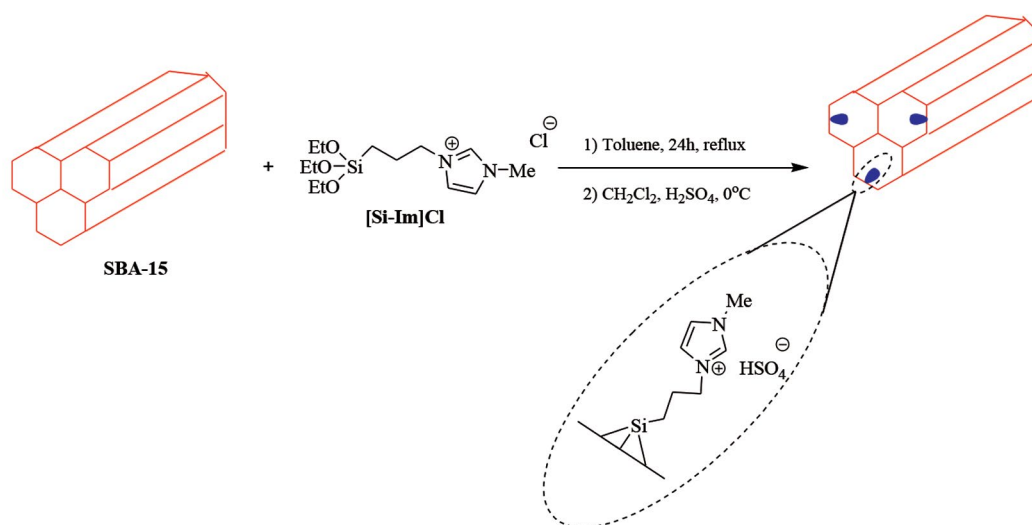
To an aqueous solution of NaCl (1 M, 25 mL) with an initial pH 5.9, the [SBAIm]HSO₄ (100 mg) was added and the resulting mixture stirred for 24 h after which the pH of solution decreased to 2.4. This is equal to a loading of 0.99 mmol H^+ /g of acidic catalyst [26,27].

RESULTS AND DISCUSSION

There have been few studies about the preparation of silica supported acidic ionic liquid catalyst and its application for nucleophilic substitutions. Recently, we have focused on developing novel PTC systems for organic transformations and also successfully performed the one-pot synthesis of phthalazinedione and phthalazinetrione heterocyclic compounds with [SBAIm] HSO_4 composite on SBA-15 mesoporous silica as support [24]. For [SBAIm] HSO_4 , the surface of the mesoporous silica was modified by reaction with the ionic liquid 1-(triethoxysilylpropyl)-3-methylimidazolium hydrogen sulfate (IL- HSO_4).

Herein, we report catalytic application of [SBAIm] HSO_4 as a catalyst for the facile preparation of benzyl thiocyanates and azides by nucleophilic substitution reaction of benzyl halides.

First, the [SBAIm]HSO₄ was prepared according to our reported method as shown in Scheme 2. The catalyst has been characterized by FT-IR (Fig. 1), SEM (Fig. 2), TEM (Fig. 3), TGA and DTG (Fig. 4), and by their comparisons with that of authentic sample.



Scheme 2. Synthesis of [SBAIm] HSO_4 .

The FT-IR analysis of SBA-15 and [SBA-Im]HSO₄ exhibit basic characteristic peaks at 460, 805, 950, and 1092 cm⁻¹, most probably attributable to symmetric and asymmetric stretching vibrations of Si-O bonds.

The C-H stretches peaks at 1200 to 1250 and 2950 to 2830 cm⁻¹ indicate that the surface of porous silica is successfully modified by 1-(triethoxysilylpropyl)-3-methylimidazolium hydrogen sulfate.

Characteristic peaks of [SBA-Im]HSO₄, at approximately 1568 and 1644 cm⁻¹ were attribute to C=C and C=N stretching vibrations, respectively, of the imidazole ring, and a band at approximately 1465 cm⁻¹ was characteristic of the tertiary amine group. The broad band at approximately 3450 cm⁻¹ was ascribed to the stretching vibrations of the SiO-H bond and the HO-H vibration of water molecules adsorbed on the silica surface. The band at approximately 1635 cm⁻¹ was also ascribed to the bending vibration of water molecules adsorbed on the surface.

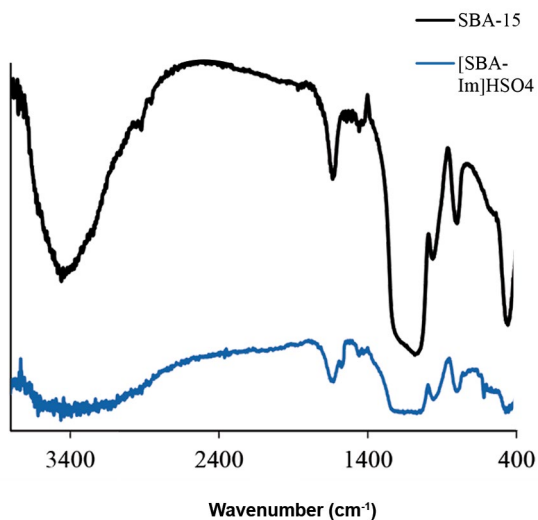


Fig. 1. The FT-IR spectra of SBA-15 and [SBA-Im]HSO₄.

Scanning electron microscopy (SEM) is a useful tool for determining the size distribution and particle shape. The morphological features of [SBA-Im]HSO₄ were studied by SEM and TEM (Fig. 2 and 3). From the TEM image, the hexagonal pore structure and orderly pore arrangement could

be clearly observed and confirmed the long-range, three dimensional, mesoporous ordering in this organocatalyst.

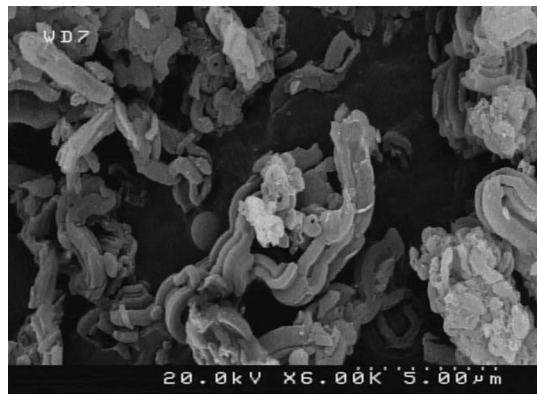


Fig. 2. The SEM image of [SBA-Im]HSO₄.

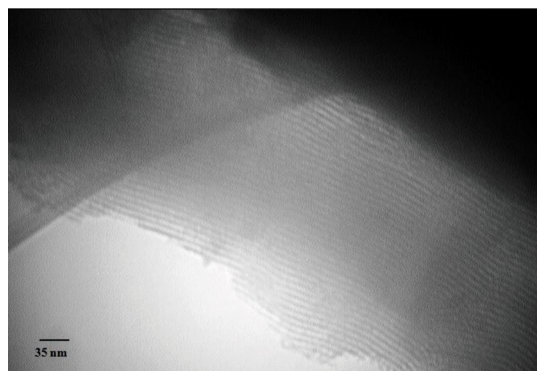


Fig. 3. The TEM image of [SBA-Im]HSO₄.

Figure 4 shows TGA thermogram of the [SBA-Im]HSO₄. The [SBA-Im]HSO₄ hybrid material loses most of the weakly bonded water molecules below 200 °C. Secondary weight losses at approximately 200 and 590 °C are a result of decomposition of the organic components of [Si-Im]HSO₄.

After characterization, in order to investigate the possible catalytic properties of [SBA-Im]HSO₄ in the nucleophilic substitution reaction, the reaction of benzyl halides with azide anion in water have been chosen.

Initially, the mixture of benzyl chloride and NaN₃ in water have been chosen as the model reaction to determine whether the use of the organocatalyst was

efficient and to investigate the optimal conditions. After some experiments, it was found that the use of 1.5 equiv. of NaN_3 per benzyl chloride in the presence of $[\text{SBA-Im}]\text{HSO}_4$ in the water were the best conditions and after stirring for 25 min at 90 °C, the clean formation of a product was observed. It should be pointed out that in the absence of $[\text{SBA-Im}]\text{HSO}_4$, the reaction was sluggish (27% yield) and even after prolonged reaction time (60 min) a considerable amount of starting material was remained. Moreover, the reaction mixture was contaminated with benzyl alcohol.

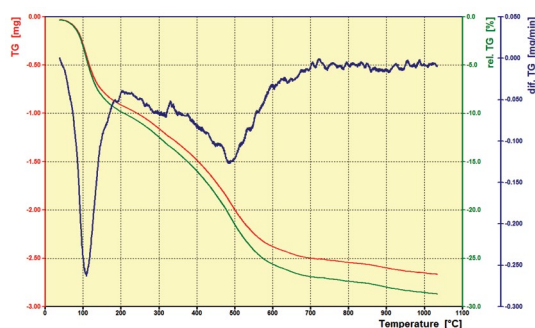


Fig. 4. TGA-DTG of $[\text{SBA-Im}]\text{HSO}_4$.

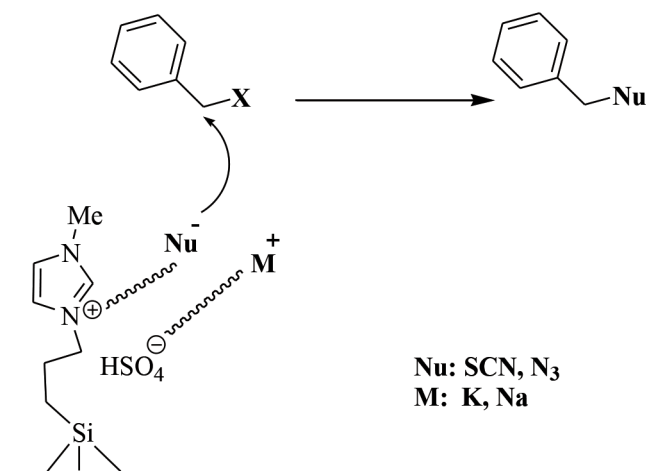
We have examined the catalytic ability of $[\text{SBA-Im}]\text{HSO}_4$ for conversion of benzyl halides to benzyl azides with NaN_3 in water at 90 °C. This catalyst acted very efficiently and it converts different benzyl halides to their corresponding benzyl azides

in high isolated yields. The obtained results of the reaction are given in Table 1.

After the success of this first set of nucleophilic substitution reaction catalyzed by $[\text{SBA-Im}]\text{HSO}_4$ in water, we focused our attention on the other nucleophilic substitution reaction, conversion of benzyl halides to the corresponding thiocyanates. Thus, various benzylic halides were treated with thiocyanate anion under the optimized reaction condition for azide anion (Scheme 3) (Table 2). Similar to azide anion, in the absence of $[\text{SBA-Im}]\text{HSO}_4$, the reaction of benzyl chloride and thiocyanate anion had 23% yield, and even after prolonged reaction time (80 min) a considerable amount of starting material was remained. The desired products were formed in high yields and side products such as isothiocyanates were not observed. ^{13}C resonance of the $-\text{SCN}$ and $-\text{NCS}$ groups at ~ 111 and ~ 145 ppm, respectively, are very characteristic for thiocyanate and isothiocyanate functionalities [20].

To investigate the constancy of catalyst activity, the reusability of the catalyst in the reaction of benzyl chloride and NaN_3 in water was evaluated. The catalyst was recovered after each run, washed with hot ethanol, dried and tested for its activity in the subsequent run. The results were shown that the catalyst does not show any loss in its activity and produced product in 90, 89, 89 and 87 % yield, respectively.

This organic-inorganic hybrid catalyst contains an acidic ionic liquid. It is thought that organic ionic liquid can enhance the hydrophobicity as well as the hydrophilicity of silica cavities and, therefore, that it can be used as a phase transfer catalyst in the nucleophilic substitution of benzyl halides in water (Scheme 3).



Scheme 3. Postulated roles of $[\text{SBA-Im}]\text{HSO}_4$ in the nucleophilic substitution.

Table 1. Nucleophilic substitution reaction of benzyl halides with azide anion in water catalyzed by [SBA-Im]HSO₄

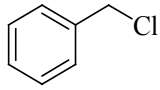
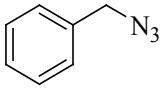
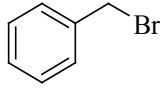
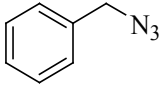
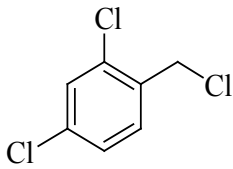
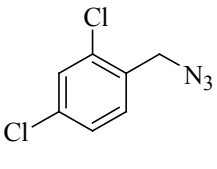
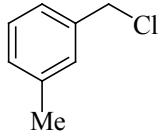
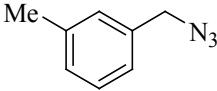
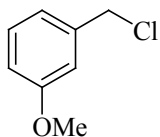
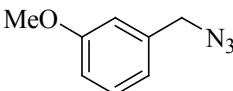
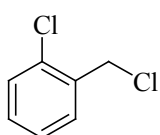
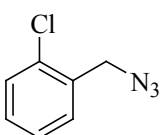
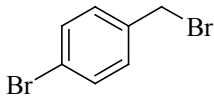
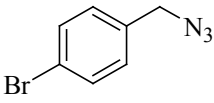
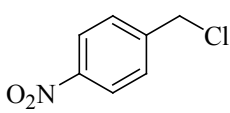
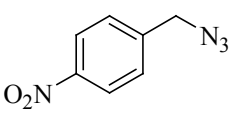
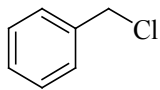
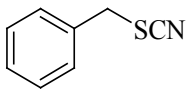
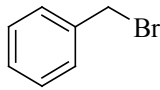
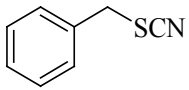
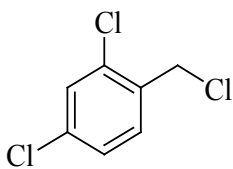
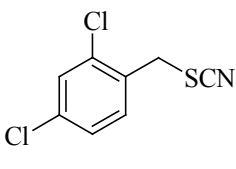
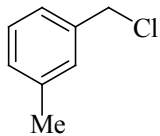
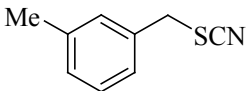
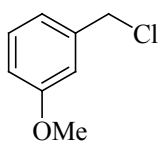
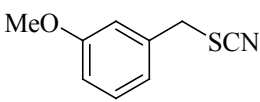
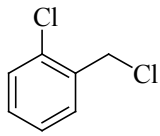
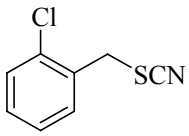
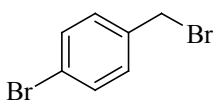
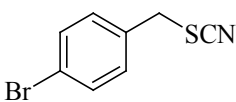
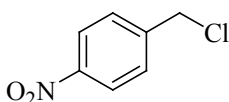
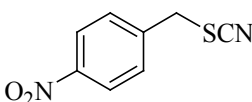
Entry	Benzyl halide	Product	Time (min)	Yield (%)
1			25	90
2			15	89
3			50	87
4			20	89
5			40	86
6			40	87
7			110	80
8			30	83

Table 2. Nucleophilic substitution reaction of benzyl halides with thiocyanate anion in water catalyzed by [SBA-Im]HSO₄

Entry	Benzyl halide	Product	Time (min)	Yield (%)
1			60	90
2			60	92
3			75	86
4			60	87
5			60	86
6			60	86
7			150	85
8			150	85

CONCLUSION

In this study, the performance of [SBA-Im] HSO₄ as an acidic phase-transfer catalyst for nucleophilic substitution reactions of benzyl halides with potassium thiocyanate and sodium azide in water have investigated. The catalyst was characterized by FT-IR, TGA-DTA, SEM, and TEM. The most important features of this method are high yields, clean reactions and the catalyst can be recovered and recycled, which make it a useful and attractive process for synthesis of benzyl azides and thiocyanates.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1. J. Miao, H. Wan, G. Guan, *Catal. Commun.* 12, 353 (2011).
2. A. S. Amarasekara, O. S. Owereh, *Catal. Commun.* 11, 1072 (2010).
3. A. Pourjavadi, S. H. Hosseini, R. Soleyman, *J. Mol. Catal. A Chem.* 365, 55 (2012).
4. J. Zhu, B. He, J. Huang, C. Li, HYPERLINK "http://www.sciencedirect.com/science/article/pii/S138718111730690X" \l "" T. Ren *Microporous Mesoporous Mater.* 260, 190 (2018).
5. S. Zhang, H. Gao, J. Li, Y. Huang, A. Alsaedi, T. Hayat, X. Xu, HYPERLINK "http://www.sciencedirect.com/science/article/pii/S030438941630807X" \l "" X. Wang, *J. Hazard. Mater.* 321, 92 (2017).
6. V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J. M. Basset, *Chem. Rev.* 111, 3036 (2011).
7. E. Dana, A. Sayari, *Chem. Eng. J.* 166, 445 (2011).
8. F. Gao, J. Hu, C. Peng, H. Liu, Y. Hu, *Langmuir* 28, 2950 (2012).
9. S. K. Badamali, R. Luque, J. H. Clark, S. W. Breeden, *Catal. Commun.* 31, 1 (2013).
10. B. Zou, Y. Hu, D. Yu, L. Jiang, W. Liu, P. Son, *Colloids Surf. B* 88, 93 (2011).
11. A HYPERLINK "http://www.tandfonline.com/author/Coriolano%2C+Ana+C+F". C. F. Coriolano, HYPERLINK "http://www.tandfonline.com/author/Barbosa-%2C+Gabriel+F+S" G. F. S. Barbosa, HYPERLINK "http://www.tandfonline.com/author/Alberto%2C+Cleyton+K+D" C. K. D. Alberto, HYPERLINK "http://www.tandfonline.com/author/Delgado%2C+Regina+C+O+B" R. C. O. B. Delgado, HYPERLINK "http://www.tandfonline.com/author/Castro%2C+Kesia+K+V" K. K. V. Castro, HYPERLINK "http://www.tandfonline.com/author/Araujo-%2C+Antonio+S" A. S. Araujo, *Pet. Sci. Technol.* 34, 627 (2016).
12. Y. Yang, G. Lv, L. Deng, B. Lu, J. Li, J. Zhang, J. Shi, S. Du, *Microporous Mesoporous Mater.* 250, 47 (2017).
13. H. Mahdavi, B. Tamami, *React. Funct. Polym.* 64, 179 (2005).
14. S. Xue, S. Ke, T. Wei, L. Duan, Y. Guo, *J. Chin. Chem. Soc.* 51, 983 (2004).
15. E. Aly, M. Abdo, A. El-Gharably, *J. Chin. Chem. Soc.* 51, 1013 (2004).
16. D. C. M. Albanese, F. Foschi, M. Penso, *Org. Process Res. Dev.* 20, 129 (2016).
17. R. G. Guy, S. Patai, *The Chemistry of the Cyanates and Their Thio Derivatives*, Wiley Interscience, New York (1977).
18. O. Prakash, H. Kaur, H. Batra, N. Rani, S.P. Singh, R.M. Moriarty, *J. Org. Chem.* 66, 2019 (2001).
19. A. R. Kiasat, S. Nazari, J. Davarpanah, *C. R. Chimie.* 17, 124 (2014).
20. HYPERLINK "http://pubs.rsc.org/en/results?searchtext=Author%3AThomas%20Castanheiro" T. Castanheiro, HYPERLINK "http://pubs.rsc.org/en/results?searchtext=-Author%3AJean%20Suffert" J. Suffert, HYPERLINK "http://pubs.rsc.org/en/results?searchtext=Author%3AMorgan%20Donnard" M. Donnard, HYPERLINK "http://pubs.rsc.org/en/results?searchtext=Author%3AMihaela%20Gulea" M. Gulea, *Chem. Soc. Rev.* 45, 494 (2016).
21. HYPERLINK "http://pubs.acs.org/author/Wang%2C+Chen-Gang" C. G. Wang, HYPERLINK "http://pubs.acs.org/author/Goto%2C+Atsushi" A. Goto, *J. Am. Chem. Soc.* 139, 10551 (2017).
22. J. Davarpanah, A. R. Kiasat, S. Noorizadeh, M. Ghahremani, *J. Mol. Catal. A* 376, 78 (2013).
23. J. Davarpanah, A. R. Kiasat, *Catal. Commun.* 41, 6 (2013).
24. J. Davarpanah, P. Rezaee, S. Elahi, *Res. Chem. Intermed.* 41, 9903 (2015).
25. D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* 279, 548 (1998).
26. B. Karimi, H. M. Mirzaei, A. Mobaraki, *Catal. Sci. Technol.* 2, 828 (2012).
27. B. Karimi, H. M. Mirzaei, *RSC Adv.* 3, 20655 (2013).