

## Research Article

# Al-MCM-41: An Efficient and Recyclable Heterogeneous Catalyst for the Synthesis of $\beta$ -Hydroxy Thiocyanates in Water

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An efficient and green procedure has been developed for the synthesis of  $\beta$ -hydroxy thiocyanate by the regioselective ring opening of epoxides with  $\text{NH}_4\text{SCN}$ . The reaction was carried out in water without any organic solvent at  $40^\circ\text{C}$ , using Al-MCM-41 (a mesoporous aluminosilicate) as catalyst. In this method, several types of epoxides carrying electron-donating or withdrawing groups were rapidly converted to the corresponding  $\beta$ -hydroxy thiocyanates in good from excellent yields. Various advantages associated with this protocol include simple workup procedure, short reaction times, high product yields, greater regioselectivity, and easy recovery and reusability of the catalyst.

## 1. Introduction

Chemical processes employ large amounts of hazardous and toxic solvents. One of the challenges for the chemists is to come up with new approaches that are less hazardous to human and environment. The choice of pursuing a low waste route and reusable reaction media and minimizing the economic cost and environmental impact of a chemical process is becoming ever more urgent for the future. One of the most promising approaches uses water as reaction medium. Water is an abundant, cheap, nontoxic, and nondangerous solvent [1].

From green chemistry point of view, there is an increasing demand for transformation of homogeneous into heterogeneous catalysis in organic synthesis, especially in fine chemical synthesis due to the ease with which catalysts can be separated from products and recycled [6]. Micro- and mesoporous materials offer unique opportunities for heterogeneous catalysis by their large surface area. Recently, a wide range of acid-base or redox catalysts have been developed by modification of such material via introducing active elements inside the pore walls [7, 8]. Mesoporous aluminosilicate, Al-MCM-41, is well known to show remarkable

acidic properties. Since its pore sizes are larger than those of zeolites, bulky organic substrates can contact acid sites of mesoporous aluminosilicates [9]. Therefore, Al-MCM-41 molecular sieves have been shown to catalyze several organic transformations under vapor or liquid phase reaction conditions [10–12].

Because of the importance of  $\beta$ -hydroxy thiocyanates in the field of synthetic organic chemistry [13] and in continuation of our ongoing effort to introduce novel catalysts for organic transformation [14–18], in this project we decided to explore the use of nanosized Al-MCM-41 as an efficient catalyst for the synthesis of  $\beta$ -hydroxy thiocyanates by the regioselective ring opening of epoxides under mild and ecofriendly conditions (Scheme 1).

## 2. Result and Discussion

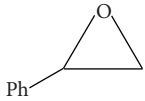
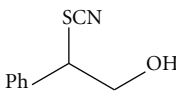
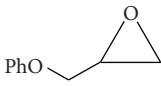
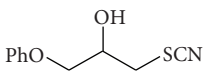
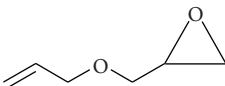
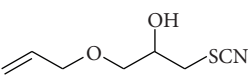
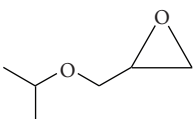
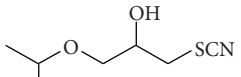
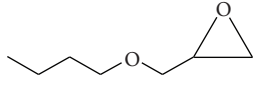
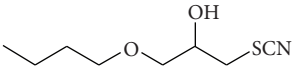
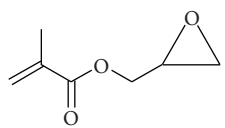
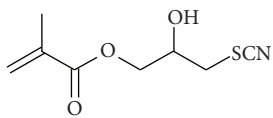
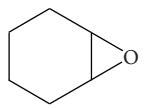
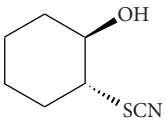
First, the Al-MCM-41 was prepared in our laboratory according to the reported method (Figure 1) [19].

Then, the Al-MCM-41-catalyzed ring opening of epoxide was applied to synthesis of various  $\beta$ -hydroxy thiocyanates in the presence of thiocyanate anion in water. The reaction was

TABLE 1: Optimization of reaction condition for thiocyanation of phenyl glycidyl ether (1 mmol).

Entry	Al-MCM-41/mg	NH <sub>4</sub> SCN/mmol	Condition	Time (min)	Conversion
1	0	3	reflux	60	—
2	100	3	r.t	60	70
3	100	3	40°C	30	100
4	100	2	40°C	30	65
5	50	3	40°C	30	45
6	80	3	40°C	30	70

TABLE 2

Entry	Epoxide	Product <sup>a</sup>	Time (min)	Yield <sup>b</sup> (%)
1		 <b>1b</b>	35	88
2		 <b>2a</b>	30	90
3		 <b>3a</b>	30	83
4		 <b>4a</b>	30	85
5		 <b>5a</b>	25	80
6		 <b>6a</b>	30	82
7		 <b>7a</b>	20	80

<sup>a</sup> Products are known and were identified by comparison of FT-IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectral data with those of authentic samples [2–5].

<sup>b</sup> Isolated yields.

optimized with respect to the amount of catalyst, thiocyanate salt, and appropriate temperature. The results are recorded in Table 1. On the basis of the experiments performed, we obtained the best results with 0.1 g Al-MCM-41 and 3 mmol NH<sub>4</sub>SCN at 40°C (Table 1, entry 3).

Under optimized reaction conditions, several types of epoxides carrying electron-donating or with-drawing groups were rapidly converted to the corresponding product from good to excellent yields in aqueous media at 40°C. The results are summarized in Table 2.

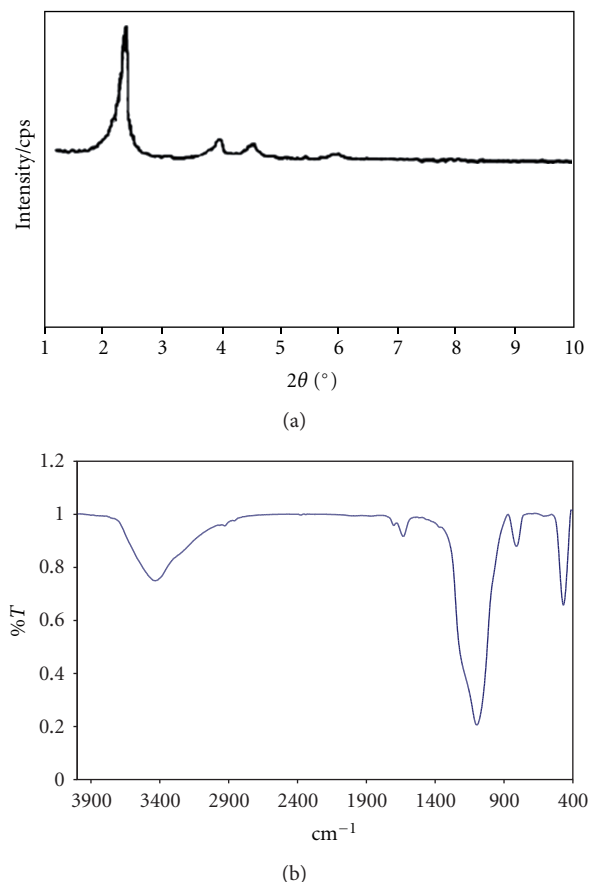


FIGURE 1: X-ray diffractogram and FTIR spectra of Al-MCM-41.

In the present conversion, epoxide is activated by the acidic proton of Al-MCM-41, which undergoes a nucleophilic attack by  $\text{SCN}^-$  anion (Scheme 2).

In all cases, very clean reactions were observed, and the structures and the regiochemical ratios of products were determined by FT-IR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectroscopy and also by comparison with authentic compounds. It is also worth mentioning that the Al-MCM-41 catalyst was easily recovered by simple filtration, and showed no appreciable loss of activity and without any variation in the reaction times or the yields of the corresponding products when recycled several times (Figure 2).

In conclusion, we have developed a novel, facile and efficient ring opening of epoxides that with  $\text{SCN}^-$  as nucleophiles in the presence of Al-MCM-41. Mild reaction condition, simplicity in operation, low environmental impact and high yields of products can be considered as an advantage of this method.

### 3. Experimental

**3.1. General Comments.** Products were characterized by comparison of their physical data, IR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectra with known samples. NMR spectra were

recorded in  $\text{CDCl}_3$  on a Bruker Avance DPX 400 MHz spectrometer using TMS as an internal standard. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrometer.

**3.2. Synthesis of Al-MCM-41.** Al-MCM-41 were syntheses starting from a mixing solution of NaOH (4.04 g in 120 mL distilled water) and silicic acid (16.08 g) at  $75^\circ\text{C}$  for 1 h and then, it was slowly added to cetyltrimethyl ammonium bromide (9.0 g) under vigorous stirring. After 1 hour, this solution was added to an aqueous suspension of aluminum sulfate drop by drop under continuous stirring. The resultant gel was transferred into a teflon-lined stainless steel autoclave under autogenous pressure and treated hydrothermally at  $110^\circ\text{C}$  for 4 days. The solid product was obtained after cooling to room temperature, filtering, washing, and drying at  $110^\circ\text{C}$  for 6 hours. Finally, the product was calcined at  $500^\circ\text{C}$  for 5 hours.

**3.3. Typical Procedure for the Preparation of  $\beta$ -Hydroxy Thiocyanates Catalyzed by Al-MCM-41.** Epoxide (1.0 mmol) was added to a suspension of Al-MCM-41 (100 mg), which was pretreated in vacuo at  $120^\circ\text{C}$  for 1 hour and  $\text{NH}_4\text{SCN}$  (228 mg, 3.0 mmol) in water (5 mL). The mixture was magnetically stirred at  $40^\circ\text{C}$  for the time shown in Table 1. After complete consumption of epoxide as judged by TLC (using *n*-hexane/ethylacetate (5: 1) as eluent), the insoluble Al-MCM-41 catalyst was filtered off and the filtrate was extracted with ether (3  $\times$  5). The extract was dried over  $\text{Na}_2\text{SO}_4$  and evaporated in vacuo to give the alcohols. The crude products were purified by silica gel column chromatography.

**3.4. Spectral Data.** *2-Hydroxy-1-phenylethyl thiocyanate 1b*: IR  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2151 (SCN);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  4.15–4.32 (1H, m), 4.42 (1H, m), 4.62 (1H, m), 4.85 (1H, s), 7.32–7.52 (5H, m, Ar-H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  46.34 ( $\text{CH}_2\text{SCN}$ ), 59.70 (CHOH), 110.58 (SCN), 128.57 (*o*-CH), 129.83 (*p*-CH), 129.94 (*m*-CH), 137.43 (C).

*3-Phenoxy-2-hydroxypropyl thiocyanate 2a*: IR  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2156 (SCN);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  3.30 (2H, d,  $\text{CH}_2\text{SCN}$ ), 3.78 (1H, s, OH), 4.15 (2H, d,  $\text{OCH}_2$ ), 4.29 (1H, m,  $\text{CHOH}$ ), 6.95 (2H, m, Ar-H), 7.02 (1H, m, Ar-H), 7.28 (2H, m, Ar-H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  37.4 ( $\text{CH}_2\text{SCN}$ ), 68.1 (CHOH), 69.5 ( $\text{OCH}_2$ ), 113.0 (SCN), 114.6 (*o*-CH), 121.3 (*p*-CH), 129.9 (*m*-CH), 158.5 (C).

*3-Allyloxy-2-hydroxypropyl thiocyanate 3a*: IR  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2155 (SCN);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  3.04 (1H, s, OH), 3.24 (2H, d,  $\text{CH}_2\text{SCN}$ ), 3.53 (2H, d,  $\text{OCH}_2$ ), 4.05 (3H, m,  $\text{OCH}_2\text{CHOH}$ ), 5.19–5.29 (2H, m, = $\text{CH}_2$ ), 5.87 (1H, m, =CH);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  37.3 ( $\text{CH}_2\text{SCN}$ ), 69.2 ( $\text{CH}_2\text{O}$ ), 71.1 (CHOH), 71.6 ( $\text{OCH}_2$ ), 113.1 (SCN), 117.5 ( $\text{CH}_2=$ ), 133.7 (=CH).

*2-Hydroxy-3-isopropoxypropyl thiocyanate 4a*: IR  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2156 (SCN);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.18 (6H, d,  $\text{CH}_3$ ), 2.7 (1H, m), 3.1 (1H, m), 3.18 (1H, m), 3.45 (1H, m), 3.58 (1H, m), 4.1 (1H, m);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100

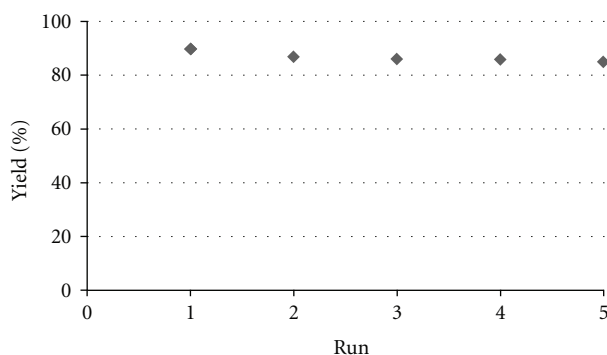
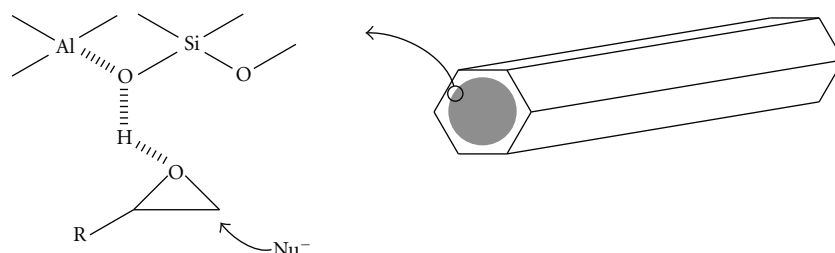
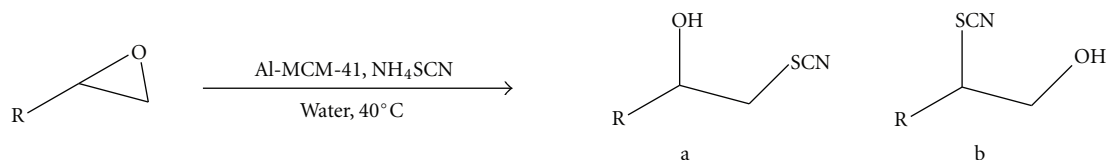


FIGURE 2: Synthesis of 3-phenoxy-2-hydroxypropyl thiocyanate with recovered Al-MCM-41.

MHz):  $\delta$  21.90 ( $\text{CH}_3$ ), 37.29 ( $\text{CH}_2\text{-SCN}$ ), 69.36 ( $\text{CHOH}$ ), 72.55 ( $\text{CH}_2\text{O}$ ), 76.60 ( $\text{CH}$ ), 112.49 ( $\text{SCN}$ ).

**3-Butoxy-2-hydroxypropyl thiocyanate 5a:** IR  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2156 ( $\text{SCN}$ );  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  0.95 (3H, t,  $\text{CH}_3$ ), 1.52–1.41 (4H, m,  $\text{CH}_2\text{-CH}_2$ ), 2.80 (1H, m,  $\text{OH}$ ), 3.10 (2H, m,  $\text{CH}_2\text{SCN}$ ), 3.55 (4H, m,  $\text{CH}_2\text{-O-CH}_2$ ), 4.15 (1H, m,  $\text{CH-OH}$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  13.85 ( $\text{CH}_3$ ), 19.22 ( $\text{CH}_2\text{-CH}_3$ ), 31.50 ( $\text{CH}_2\text{-CH}_2$ ), 37.25 ( $\text{CH}_2\text{SCN}$ ), 69.15 ( $\text{CH-OH}$ ), 71.50 ( $\text{CH}_2\text{O}$ ), 72.0 ( $\text{CH}_2\text{CHOH}$ ), 112.48 ( $\text{SCN}$ ).

**2-Hydroxy-3-thiocyanatopropyl methacrylate 6a:** IR  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2157 ( $\text{SCN}$ );  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.85 (3H, m,  $\text{CH}_3$ ), 3.01–3.18 (2H, d,  $\text{CH}_2\text{SCN}$ ), 3.40 (1H, m,  $\text{CHOH}$ ), 4.13 (1H, s,  $\text{OH}$ ), 4.15 (2H, d,  $\text{OCH}_2$ ), 5.56 (1H, m,  $=\text{CH}_2$ ), 6.07 (1H, m,  $=\text{CH}_2$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  18.4 ( $\text{CH}_3$ ), 37.3 ( $\text{CH}_2\text{SCN}$ ), 66.1 ( $\text{OCH}_2$ ), 68.1 ( $\text{CHOH}$ ), 112.8 ( $\text{SCN}$ ), 126.6 ( $\text{CH}_2=$ ), 135.2 ( $=\text{CH}$ ), 167.1 ( $\text{C=O}$ ).

**2-Hydroxycyclohexyl thiocyanate 7a:** IR  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2151 ( $\text{SCN}$ );  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.21–1.29 (4H, m,  $\text{CH}_2\text{CH}_2\text{CHSCN}$ ), 1.69 (2H, m,  $\text{CH}_2\text{CH}_2\text{CHOH}$ ), 1.98 (2H, m,  $\text{CH}_2\text{CHOH}$ ), 3.14 (1H, s,  $\text{OH}$ ), 3.16 (1H, m,  $\text{CHSCN}$ ),

3.34 (1H, m,  $\text{CHOH}$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  23.1 ( $\text{CH}_2\text{CH}_2$ ), 25.2 ( $\text{CH}_2\text{CH}_2$ ), 30.0 ( $\text{CH}_2\text{CHSCN}$ ), 31.4 ( $\text{CH}_2\text{CHOH}$ ), 51.5 ( $\text{CHSCN}$ ), 79.1 ( $\text{CHOH}$ ), 110.6 ( $\text{SCN}$ ).

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