Journal of Molecular Catalysis A: Chemical 379 (2013) 68–71

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Tuning the catalytic activity of lanthanide-organic framework for the cyanosilylation of aldehydes

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ARTICLE INFO

Article history:
Received 27 June 2012
Received in revised form 23 July 2013
Accepted 28 July 2013
Available online 12 August 2013

Keywords:
Cyanosilylation of aldehyde
Heterogeneous catalysis
Lanthanide
Metal-organic framework
MOF

ABSTRACT

Lanthanide-organic framework (LnMOF) $[Eu_2(MELL)(H_2O)_6]$ (1) was rapidly produced via microwave-assisted hydrothermal synthesis and its performance as heterogeneous catalyst for the cyanosilylation of aldehydes was investigated. The catalytic assays were performed with different aldehydes and solvents using as-prepared and thermally active (100 °C for 1 h) LnMOF material, and the results show that (**1**) acts as an excellent catalyst for the addition of trimethylsilyl cyanide to aldehydes with short reaction times and excellent yields. In addition, the catalyst was recycled and recovered in the addition reaction of TMSCN to 2-furfuraldehyde without loss of activity.

1. Introduction

Metal-organic frameworks (MOFs), which are also known as coordination polymers (CPs), are a class of crystalline compounds that have been extensively studied in the last twenty years [1]. The worldwide interest is motivated by the almost infinite possibilities for framework construction, wide superficial area, porosity and potential applications in catalysis [2], luminescence [3], sensor [4], magnetism [5], gas storage [6], drug delivery [7] and optoelectronics [8]. MOFs have proved to be very useful in heterogeneous catalysis, because they combine advantages, such as facile separation and recovery of the catalyst as well as high stability and ease of handling [9]. In addition, the MOF pores may be systematically tailored for specific catalytic applications [10]. These characteristic provide good justification for the growing interest in MOFs as heterogeneous catalysts in organic reactions [2b,11].

Lanthanide compounds have been extensively used as Lewis acids in various reactions including asymmetric catalysis. The most common application appears in homogeneous catalysis with the use of chloride [12], triflates [13], p-toluenesulfonates [14], dithiocarbamate complexes [15], alkoxides [16] and others compounds [17]. The addition of cyanide to a carbonyl compound to form a cyanohydrin is one of the fundamental carbon-carbon bond forming reactions in organic chemistry [18]. It is important to note that the enantioselective synthesis of cyanohydrin represents a useful route for the production of important organic intermediates, such as α-hydroxyl acids and their derivatives as well as β-amino alcohols [19]. The most commonly used alternative cyanide source is trimethylsilyl cyanide (TMSCN). Catalysis with TMSCN can also be induced thermally or by an enormous range of catalysts including Lewis acids, bases and nucleophiles [20]. The Lewis acid used for the addition of TMSCN in aldehydes and ketones primarily includes compounds based on transition metals [20] including MOFs [21] and lanthanides metal compounds [15,20,22]. Therefore, lanthanide-organic frameworks (LnMOFs) exhibit great potential as Lewis acids in heterogeneous catalysis. While catalysis is one of the most promising applications of LnMOFs, only a few examples have been reported to date. Recently, $[Ln_2(MELL)(H_2O)_6]$ materials (where $Ln^{3+} = La^{3+}$, Eu^{3+}, Tb^{3+} and Gd^{3+}) have been synthesized and were used as light-conversion molecular devices (LCMDs) and a contrast agent for magnetic resonance imaging (MRI) [23]. However, to date, investigations of their catalytic activities are non-existent. Therefore, we report on the performance of $[Eu_2(MELL)(H_2O)_6]$ as a heterogeneous catalyst for the cyanosilylation of aldehydes (Scheme 1).

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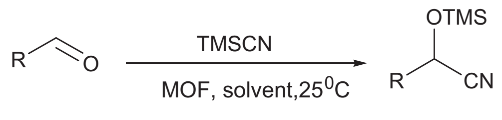
http://dx.doi.org/10.1016/j.molcata.2013.07.016



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Scheme 1.

2. Experimental

2.1. Synthesis of europium organic-framework

An equimolar mixture (0.85 mmol) of mellitic acid (Mell), $Eu(NO_3)_3{\cdot}6H_2O$ and H_2O (4.0 mL) in a 10.0 mL IntelliVent reactor was placed inside a CEM Focused Microwave^{TM} Synthesis System Discover S-Class apparatus. The reactions proceeded at 180 °C over 20 min under constant magnetic stirring. The final materials were obtained in a yield of ca. 60% after being washed with water, acetone and air-dried. The powder synchrotron X-ray diffraction patterns were acquired at ambient temperature (300 K) in a 2θ range of 8–25° using a Huber diffractometer in high resolution mode (low intensity, $E = 10$ keV) on a multi-purposed powder station D10A-XRD2 beam line at the Brazilian Synchrotron Light Laboratory (LNLS). Variable-temperature powder X-ray diffraction data for $[Eu_2(MELL)(H_2O)_6]$ **(1)** were collected using a Bruker D8 Advanced with DaVinci design equipped with a LynxEye Linear Position Sensitive Detector and a copper (Cu) sealed tube ($\lambda k\alpha_1 = 1.5404$ Å, $\lambda k\alpha_2 = 1.5444$ Å, $I\alpha_2/I\alpha_1 = 0.5$) fitted with an Anton Parr HKL 16 high-temperature chamber controlled by an Anton Parr 100 TCU unit. The sample was submitted at 30, 100, 125 and 150 °C for a period of 1 h prior to data collection. The intensity data were collected in the step mode (0.02°, 5 per step) in the range of ca. $10 \leq 2\theta° \leq 48$. The Rietveld refinements [24] for $[Eu_2(MELL)(H_2O)_6]$ were performed with the software GSAS/EXPGUI [25] using the atomic coordinates of the structural model previously reported as a starting guess [23a]. The preferential orientation was corrected using the spherical harmonic model (sixth order) proposed by Jarvinen [26], the peak profile was adjusted using the Thompson-Cox-Hastings function modified by Young and Desai (pV-TCHZ) [27], the surface roughness correction was refined using the Pitschke function and the background was fitted by an eighth-degree shifted Chebyshev polynomial function. In the final runs, the following parameters were refined: scale factor, background and absorption coefficients, spherical harmonic, unit-cell parameters and pV-TCHZ correction for the asymmetric parameters.

2.2. General procedure for cyanosilylation of aldehydes

$[Eu_2(MELL)(H_2O)_6]$ preheated at 100 °C for 1 h (10.0 mg) in acetonitrile (3.0 mL) at room temperature was added to the aldehyde (0.125 mmol) followed by TMSCN (0.25 mmol). The resulting solution was stirred at room temperature for 1 h prior to quenching with H_2O (10.0 mL). The mixture was diluted with dichloromethane (15 mL), the organic phase was isolated, the organic extracts were dried over anhydrous Na_2SO_4 and the solvent was removed in vacuum. When necessary, the crude product was purified via flash column chromatography (30% ethyl acetate/hexanes as eluent) to afford the product as an oil. The conversion to the corresponding O-trimethylsilyl ethers cyanohydrins was analyzed by gas chromatography coupled with a mass spectrometer. All of the compounds were characterized by comparison with previously reported spectral data.

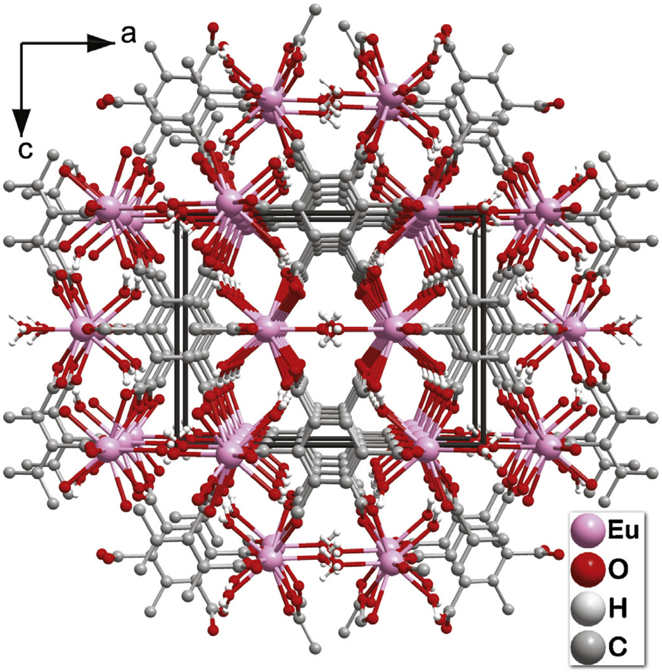

Fig. 1. Three-dimensional structure of **(1)**. View along the *b*-axis.

3. Results and discussion

The $[Eu_2(MELL)(H_2O)_6]$ structure is basically a three-dimensional framework (Fig. 1) with a one-dimensional channel system running parallel to the *b*-axis [19].

Fig. 2 shows the Rietveld refinement for **(1)** treated at 100 °C for 1 h, the variable-temperature powder patterns (125 and 150 °C) and the thermogravimetric curves (TGA/DTG) acquired for the as-prepared LnMOF material.

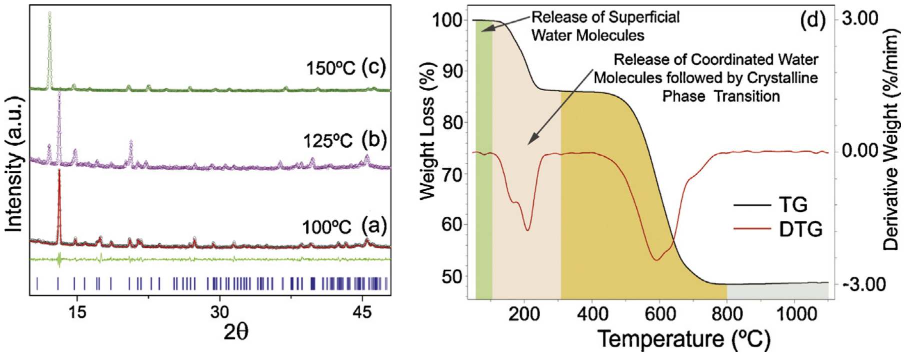

Fig. 2. (a) Final Rietveld plot of $[Eu_2(MELL)(H_2O)_6]$ **(1)** acquired after thermal treatment (100 °C for 1 h). Observed data points are indicated by black circles and the best-fit profile, difference pattern and Bragg reflections are represented as red and green solid lines and blue vertical bars, respectively. (b) and (c) Powder patterns acquired after thermal treatments at 125 and 150 °C for 1 h; (d) Thermogravimetric curves (TGA/DTG) of $[Eu_2(MELL)(H_2O)_6]$.

Table 1
Conversions *of PhCHO* to **2** catalyzed by $[Eu_2(MELL)(H_2O)_6]$.

Mass (mg)	Time (min)[#]	Conversion to 2 (%)[#]
5[*]	180	44
5[**]	180	72
–	600[***]	8[***]
10[**]	180	90
30[**]	180	100

[#] Conditions: PhCHO: TMSCN (1:2) in toluene (5.0 mL at room temperature). The conversion of PhCHO to **2** was determined by GC analysis relative to dodecane as an internal standard.

[*] As-prepared **(1)**.

[**] **(1)** thermally activated.

[***] Reaction performed without catalyst.

Table 2
Addition of TMSCN to benzaldehyde catalyzed by activated (**1**) in various solvents.

Entry	Solvent	Time (min)	Conversion to 2 (%)[#]
1	Hexane	180	34
2	Methylene chloride	90	98
3	Tetrahydrofuran	100	95
4	Acetonitrile	60	100 (45[*])
5	Ethyl alcohol	180	14
6	Water	180	0

[#] The conversion of PhCHO to **2** was determined by GC analysis relative to dodecane as an internal standard.

[*] Using $Eu(NO_3)_3{\cdot}6H_2O$ as the catalyst.

The Rietveld refinement for $[Eu_2(MELL)(H_2O)_6]$ after the first thermal treatment (Fig. 2(a)) does not show noticeable modifications in the powder pattern, which indicated that the prepared compound retained its structural integrity under this condition. The TGA/DTG results are in good agreement with the X-ray diffraction data, because a weight loss event (0.12%) was observed up to ca. 80 °C corresponding to the complete release of uncoordinated water molecules present on the crystal surface. Unlike the previously reported LnMOFs, the $[Eu_2(MELL)(H_2O)_6]$ material exhibits the presence of another crystalline phase and a phase transition collapse when maintained at 120 and 150 °C for 1 h (Fig. 2(b) and (c), respectively). However, the TGA curve does not indicate the degradation of organic residues at these temperatures. This phase transition may be attributed to the release of coordinated water molecules, because the supramolecular structure of the $[Eu_2(MELL)(H_2O)_6]$ is stabilized by hydrogen bonding interactions among the aqua ligands and the oxygen atoms from neighboring carboxylate groups. It is important to note that these results are supported by TGA/DTG. One of our main goals is to tailor the catalytic activity of $[Eu_2(MELL)(H_2O)_6]$ via surface activation, because the superficial water removal allows for the interaction between the aldehydes and the Lewis acids sites [28]. Therefore, the material was submitted to milder thermal treatment (100 °C for 1 h) to avoid the structural phase transition while exposing the Lewis acid sites.

The catalytic activities were assessed by optimized reactions between benzaldehyde and TMSCN in toluene (5.0 mL) at room temperature. The reaction times were monitored by TLC, and the conversions of benzaldehyde to O-TMS-phenylcyanohydrin-**2** were determined by gas chromatography (GC). Table 1 shows the experimental parameters, such as catalyst masses, reaction time and substrate conversions (%), for the catalytic assays.

As observed in Table 1, the reaction without the catalyst proceeded for a longer time period (10 h) and yielded only 8% of the product. However, the reactions performed in the presence of the MOF materials exhibited rapid conversion (3 h) accompanied by good product yields. Based on the same catalyst mass and reaction time, the thermally activated $[Eu_2(MELL)(H_2O)_6]$ exhibited superior catalytic activity compared to $[Eu_2(MELL)(H_2O)_6]$ (72 and 44% of substrate conversion, respectively). The effect of the amount of catalyst was investigated, and the results demonstrate that an increase in the mass of the catalyst results in an increase in the reaction yields. To investigate the effects of different solvents, substituent groups and steric hindrances of several aldehydes, we have chosen to use 10.00 mg of catalyst. In order to investigate the role of different solvents in the reaction, we have applied on the addition of TMSCN to benzaldehyde different solvents and the results are summarized in Table 2.

It is important to note that the catalyzed reactions performed in polar aprotic solvents exhibit high O-TMS-phenylcyanohydrin (**2,** R = H) yields in less than 180 min of those realized in toluene. In acetonitrile, an increase in the reaction rate was observed with complete substrate conversion in 60 min at room temperature. The yield and reaction time were higher than those obtained using $[Nd(btc)(H_2O)]$ [29] as the catalyst and $Eu(NO_3)_3{\cdot}6H_2O$. Polar protic solvents, such as water and ethyl alcohol, interfere with the reaction, because they inhibit the catalyst action by formation of hydrogen bonds with the substrate [30]. The results showed that the optimal condition for the cyanation reaction includes 10 mg of $[Eu_2(MELL)(H_2O)_6]$ in acetonitrile. Therefore, this condition was extended to reactions of other aldehydes. The results are summarized in Table 3.

As observed in Table 3, a wide variety of aldehydes can be converted to the corresponding O-trimethylsilyl cyanohydrin with good yields at room temperature. The LnMOF catalyst has exhibited a similar efficiency for the conversion of aldehydes containing activating and deactivating groups (Table 3, compounds **4**–**7**). For compound **4**, the yield and reaction time were higher than those obtained using [Tb(TCA) 4 h and 47% conversion] [31]. Similar behavior was observed for the conversion of aliphatic aldehydes (Table 3, compounds **12**–**14**). In addition, no polymerization or decomposition reactions of furfuraldehyde were detected (compound **10**). In similar compounds, the yield of ortho-substituted compounds is lower than the para-substituted compounds. 4-Hydroxy benzaldehyde is converted to the corresponding product in just 3 h (compound **7**) while 2-hydroxy benzaldehyde is converted to the corresponding product in only 6 h with 83% yield.

We investigated the potential for recycling and reuse of $[Eu_2(MELL)(H_2O)_6]$ in the addition reaction of TMSCN to 2-furfuraldehyde. The catalyst was used without pretreatment (only filtration was performed), and we found that the activated $[Eu_2(MELL)(H_2O)_6]$ could be recycled and reused at least five consecutive times without loss of activity, reaction yields or product purity. 98%, 89%, 88%, 86% and 85% of the O-trimethylsilyl cyanohydrin was isolated after the first, second, third, fourth and fifth cycles, respectively.

Table 3
Addition of TMSCN to several aldehydes catalyzed by activated (**1**).

Compound	R	Time (h)	Substrate conversion (%)[#]
3	2-Naphthyl	5	83
4	$4\text{-}NO_2\text{-}C_6H_4$	3	93
5	$4\text{-}Br\text{-}C_6H_4$	3	92
6	$4\text{-}CH_3\text{-}C_6H_4$	6	75
7	$4\text{-}OH\text{-}C_6H_4$	3	95
8	$2\text{-}OH\text{-}C_6H_4$	6	83
9	2-Pyridyl	3	62
10	2-Furfuryl	1	100
11	$5\text{-}NO_2\text{-}2\text{-}$furfuryl	3	85
12	Penthyl	3	65
13	Ethyl	3	99
14	Piperonyl	3	69

[#] Conditions: Aldehyde: TMSCN (1:2), 10 mg of activated **(1)** in acetonitrile at room temperature. The conversions of aldehydes to OTMS-cyanohydrins were determined by GC analysis relative to dodecane as an internal standard.

4. Conclusion

The LnMOF, [Eu_2(MELL)(H_2O)$_6$], was produced via microwave-assisted hydrothermal synthesis, and its performance as a heterogeneous catalyst for the cyanosilylation of aldehydes has been demonstrated. The efficacy of the catalyst increased due to surface defects induced by simple thermal treatment (100 °C for 1 h). This thermally treated catalyst has shown superior catalytic activity compared to the as-prepared material for the addition reactions of TMSN to benzaldehyde (72 and 44% of substrate conversion). [Eu_2(MELL)(H_2O)$_6$] was tested for the addition of TMSCN to various aldehydes and found to exhibit relatively high catalytic activity independent of the nature of the substituent (alkyl, aryl, activating or deactivating) or structural isomerism The catalyst was recycled several times without loss of activity, reaction yields or product purity. The reported methodology provides the first example of the application of [Eu_2(MELL)(H_2O)$_6$] as a Lewis acid heterogeneous catalyst for the cyanosilylation of carbonyl compounds.

Acknowledgments

The authors gratefully acknowledge CNPq and CAPES for their financial support and LNLS (proposal D10A-XRD2—10164) for providing the facilities.

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