



Synthesis, characterization and heterogeneous base catalysis of amino functionalized lanthanide metal-organic frameworks



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ABSTRACT

Lanthanide metal-organic frameworks (Ln-MOFs) are featured by their tolerance to water and dense structure. In this work, an amine-functionalized Ln-MOF was facilely synthesized by coordination of terbium with 2-aminoterephthalic acid under the condition of microwave irradiation. The crystal structure was characterized by single crystal X-ray diffraction, FT-IR, Raman, TG-DTA and XPS analysis. The basic catalytic activity of the NH₂-Tb-MOF was evaluated for Knoevenagel condensation and Henry reactions. Apart from the high activity and 100% selectivity to the condensation product, the NH₂-Tb-MOF catalyst could be easily recycled and reused owing to the high stability of the MOF framework formed by coordination of Tb³⁺ with carboxylic groups. Remarkably, the NH₂-Tb-MOF exhibited size-selective catalysis to substrates. For the small-sized reactants, it displayed comparable activity to the homogeneous catalyst of aniline owing to the high dispersion of NH₂- active sites and the low diffusion limits. However, in the same reaction system, extremely poor activity in Knoevenagel condensation and Henry reaction for the bulky substrate 4-(*tert*-butyl) benzaldehyde was observed due to the both effects of substitute and inhibition of diffusion into the micropores. Crystal structure analysis provided a mechanistic evidence that the heterogeneous base catalysis arose from the amino groups densely distributed inside the micropores.

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1. Introduction

Since the last decade, continual progress has given rise to thousands of metal-organic frameworks (MOFs) structures with a vast topological richness, which opened up great potential application of MOFs in gas storage and separation [1,2], catalysis [3,4], chemical sensing [5], drug delivery [6] and light harvesting [7]. With the ability to assemble organic and inorganic subunits into crystalline microporous structures, MOFs are particularly suitable for heterogeneous catalysts. This system may present the efficacy observed in homogeneous catalysts combined with the advantage that the catalyst can be easily recycled and reused because the active sites are fixed in a rigid lattice of MOFs with uniform dispersion and accessibility [8].

As an important carbon-carbon bond formation, the Knoevenagel condensation reaction has been widely used in organic synthesis [9]. The Henry (nitroaldol) reaction was conducted by a similar mechanism using different nucleophiles [10]. These

reactions were typically promoted by homogeneous basic catalysts, such as alkali metal hydroxides or amines [11]. The mechanism was referred to that the aldehyde substrate was activated by basic catalytic sites [12,13]. To address the issues of catalyst separation from the reaction system and catalyst recovery, the efficient solid catalysts, such as amine-functionalized mesoporous silicas have been widely investigated and exhibited prominent activity in the Knoevenagel condensation or Henry reaction [14]. However, preparation of these heterogeneous catalysts was generally tedious. In addition, amine grafting by adding amine functionalized alkoxy-silane reagents often led to blockage of the mesoporous channel in silicas. To maintain the accessibility of amine as catalytic centers, it was necessary to limit the loading amount of amine alkoxy-silane and thus the catalytic activity would be degraded. Metal-organic frameworks are regarded as a useful platform for implantation of amine groups due to their tunable metal clusters or nodes and flexible organic linkers [15]. Postsynthetic modification has been proposed as a facile approach to introduce the objective functional groups into MOFs structure, by which the parent MOFs could be appended a certain functional groups via one step or a series of available organic reactions [16–18]. To achieve heterogeneous basic

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catalysts, amine groups were embedded in metal centers or grafted on the frameworks of MOFs by using homogeneous amine reagents via postsynthetic modification [19]. Nevertheless, the base leaching and poor catalyst recycling were demonstrated in the amino functionalized MOFs [20,21]. On the other hand, basic MOFs could be directly synthesized by utilization of aromatic carboxylic acids attached amino groups or nitrogen heterocyclic carboxylic acid as ligands. Up to now, a series of amino-tagged MOFs such as IRMOF-3 and MIL-101(Al) have been successfully prepared [22]. These amino-MOFs suffered from low condensation reactivity due to their low pKa and low electron density caused by the two adjacent carboxylate groups which pull the electron density away from the aromatic amino groups. In addition, nitrogen-rich MOFs may also suffer from low basicity due to the competitive coordination of nitrogen with metal ions [23].

Herein, we report an amino-derived lanthanide MOF using 2-aminoterephthalic acid as ligand. Compared with amino-tagged MOFs constructed by moisture-sensitive aluminum or zinc ions as nodes, lanthanum ions (Ln^{3+}) are featured by their tolerance to water [24]. In addition, another characteristics of Ln-MOFs is the higher coordination number and the flexible and irregular coordination geometry of Ln^{3+} ions, which often results in a densely packed structure with a reduced porosity due to multiple interpenetration of network [25]. On the other hand, the compact structure of Ln-MOFs also renders a favorable dense distribution of amino groups. Meanwhile, the strong multidentate coordination between Ln^{3+} ions and carboxylate groups in Ln-MOFs may attenuate electron-withdrawing of carboxylate groups from the amino group on aromatic rings. All these effects are helpful to a robust basicity, catalytic activity and recycling of Ln-MOFs for base-catalyzed condensation reactions in aqueous medium. It is believed that with the highly ordered and crystalline structures, MOFs catalysts are easily characterized by X-ray diffraction methods in principle, which provides precise structure information of the catalytic active sites, thus allowing elucidation of structure-function relationships for the catalysts. With amino groups presented inside the micropores, the amino-tagged Ln-MOFs may have promising application in base-catalyzed Knoevenagel condensation and Henry reactions in aqueous medium.

2. Experimental section

2.1. Preparation of $\text{Tb}_2(\text{NH}_2\text{-bdc})_3(\text{DMF})_4(\text{H}_2\text{O})_2$

The amino functionalized lanthanide MOF (denoted as $\text{NH}_2\text{-Tb-MOF}$) was synthesized under the condition of microwave irradiation. The chemicals were commercially obtained and used as received. The starting reactants $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.603 g, 1.33 mmol) and 2-aminoterephthalic acid ($\text{NH}_2\text{-bdc}$, 0.363 g, 2.00 mmol) were added to a Teflon-lined vessel filled with 30.0 mL *N,N*-dimethylformamide (DMF). The solution was stirred for 10 min at ambient temperature. Then, the vessel was closed in a polytetrafluoroethylene autoclave, heated rapidly to 120 °C by microwave and kept at this temperature for 24 h. The yellow single crystals suitable for X-ray diffraction analysis were obtained. The resulting small crystals were collected and washed with distilled water and dried in air at room temperature, because they are stable in air and insoluble in water and organic solvents such as ethanol, acetonitrile, tetrahydrofuran, 1,2-dichloroethane, acetone, and *N,N*-dimethylformamide. For the purpose of catalysis application, the synthesis condition was optimized and the pure phased $\text{NH}_2\text{-Tb-MOF}$ was obtained with high yield 85% based on the above preparation of single crystal.

2.2. Single crystal X-ray structure determination

Single crystal X-ray diffraction data of the as-synthesized amino-functionalized terbium MOF were collected on a Bruker SMART diffractometer equipped with the CCD camera and graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. The quadrat crystal was mounted on a glass fiber and the data were collected at 293 K under nitrogen (data collection: $\Delta\omega = 0.60^\circ$; $2\theta = 1.73\text{--}25.01^\circ$; $\Phi = 0, 85, 170^\circ$; $\chi = 54.77^\circ$; $t = 45 \text{ s}$). The data were integrated in the Saint+ program package [26]. Empirical absorption correction was carried out by using the program SADABS [27] and refined by SHELX [28] embedded in OLEX2 [29]. In the structural model, all non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were placed in calculated positions and refined using a riding model and refined isotropically with -1.2 (-1.5 for H atoms in methyl groups) times the isotropic atomic displacement value of the atoms to hydrogen bonds. The calculation of the accessible void space to the solvent molecules was performed by PLATON program [30] using the obtained crystallographic information file (CIF).

2.3. Material characterization

Powder X-ray diffraction (PXRD) analysis was performed on a Bragg-Brentano diffractometer (Rigaku D/Max-2200) with monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) of graphite curve monochromator, 2θ in $3\text{--}50^\circ$, the step length 0.02° and scan rate $4^\circ/\text{min}$. Fourier transform infrared (FT-IR) spectra were collected at 2 cm^{-1} resolution on a Nicolet Magna 550 spectrometer (KBr, $3500\text{--}400 \text{ cm}^{-1}$). In situ variable-temperature XRD was carried out by a Buhler furnace in the temperature range of $50\text{--}900^\circ\text{C}$ under air atmosphere. The sample was smeared on a platinum sample plate and the customized temperature programming in steps of 50°C with a heating ramp of $10^\circ\text{C}/\text{min}$. Thermogravimetric and differential thermal analysis (TG/DTA) were conducted on a Shimadzu DTG-60A instrument with a heating ramp of $10^\circ\text{C}/\text{min}$ under nitrogen and oxygen atmosphere, respectively. The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ESCA). All the binding energy values were calibrated by using $\text{C}_{1s} = 284.6 \text{ eV}$ as a reference. The Tb and C, H, N contents were determined by an inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX) and an Elementar Vario EL/micro cube (German), respectively.

2.4. Catalytic activity test

The Knoevenagel condensation reaction between aldehyde and ethyl cyanoacetate (Reaction 1) and Henry reaction between aldehyde and nitromethane (Reaction 2) were used to evaluate the basic catalytic performances of $\text{NH}_2\text{-Tb-MOF}$. Prior to the experiments, the catalyst was outgassed under vacuum at 150°C for 2 h. The phase purity of $\text{NH}_2\text{-Tb-MOF}$ catalyst was confirmed by comparison of the observed and calculated PXRD patterns.

Knoevenagel condensation. The catalytic performance of $\text{NH}_2\text{-Tb-MOF}$ was tested using a series of aldehydes with ethyl cyanoacetate in different solvents. As a model system, a catalyst equivalent to 0.076 mmol amino groups, 1.0 mmol ethyl cyanoacetate and 1.2 mmol aromatic aldehyde were added in a 10 mL round-bottomed flask containing 4.0 mL distilled water and *n*-decane as an internal standard. This reaction system was stirred for 3 h at 40°C . Then, the products were extracted by ethyl acetate, followed by an analysis on a GC-17A gas chromatograph (SHIMADZU) equipped with a JWDB-5, 95%-dimethyl-1-(5%)-diphenylpolysiloxane column and a FID detector. N_2 was used as carrier gas. The column temperature was programmed from 80 to 250°C at a speed

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