

RESEARCH PAPER

Dysprosium-Organic Framework as a Heterogeneous Lewis acid Catalyst for the Sulfide Oxidation and as a precursor for the synthesis of Dy₂O₃

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ABSTRACT

Metal-organic frameworks (MOFs) are a class of hybrid porous materials made up of inorganic clusters connected with organic linkers, offering many opportunities for applications in different areas from catalysis to magnetism. A Dysprosium-organic framework was prepared by a hydrothermal reaction. The prepared MOF was characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area analysis and X-ray powder diffraction (XRD). Herein, Dy-MOF was used as a Lewis acid heterogeneous catalyst for sulfoxidation and as a precursor for the formation of micro-scale Dy₂O₃ particles. Based on the spectroscopic and microscopic analysis, Dy-MOF can catalyze the sulfide oxidation reaction to sulfoxide and the framework remains intact after the catalytic reaction. Also, the crystals of Dy-MOF turn into particles of Dy₂O₃ when heated at 650 °C in the air. This result suggests an approach for the formation of dysprosium oxide with a well-defined (uniform) morphology.

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INTRODUCTION

Metal-organic frameworks are a recently-identified class of porous polymeric material, consisting of metal ions linked together by organic bridging ligands, and are a new development on the interface between molecular coordination chemistry and materials science[1]. MOFs have interesting properties such as large exceptional tailor ability, surface areas, high porosities and the lowest densities among known crystalline materials, leading to the various applications if MOFs such as gas storage, molecular sensing and catalysis.[2] Nowadays, an increasing number of investigations have focused on the design and construction of MOFs with specific morphologies, as the size and shape of this novel type of micro/nanoscale materials are important for their wide-scope applications. Recent advances in

nanostructured MOFs have led to development of new synthesis methods that provide control over size, morphology, and nano/microstructure [3, 4].

The number of the reports on the use of MOFs as heterogeneous catalysts in organic synthesis is increasing rapidly, the target being to develop industrial processes based on these materials and has been covered in several reviews recently [5, 6]. Among these reports, MOFs with coordinatively unsaturated metal sites are particularly potent candidates for catalysis. This series of MOFs display heterogeneous Lewis acidity, due to the coordinatively unsaturated metal sites which can activate the organic molecules via metal–organic interactions in catalysis [7, 8]. Although lanthanide-organic frameworks with open lanthanide (Ln) sites are expected to be potential heterogeneous Lewis acid catalysts, reports on catalytic studies of Ln-MOFs are relatively scarce compared to the MOFs based on outer transition elements nodes

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such as zinc, cobalt, and copper [9-13].

Metal oxides are attractive for a range of applications due to their excellent chemical and thermal stability, high porosity and large surface area. They exhibit also peculiar electrical and sensing properties. Therefore, nowadays, great efforts in fundamental and applied research are dedicated to the optimization of new procedures able to synthesize pure and mixed metal oxides [14, 15]. The oxides and mixed oxides (and other compounds) of rare-earth elements are produced in varying degrees of purity from the ores Bastnäsite and monazite. Due to the Ln_2O_3 stoichiometry, these oxides are thermally very stable and have several applications in materials technology [16-19]. Recently, coordination polymers were introduced as templates for the preparation of desirable nano- and micro-scale metal-oxides [20]. There are also reports in the literature for the preparation of lanthanide oxides in which coordination polymers are used as precursors [21-23]. It has been proposed that by choosing appropriate MOF precursors with special morphologies and under suitable experimental conditions, obtaining the desired morphologies will become possible [21].

In this work, we present the synthesis and characterization of DyOF , $[\text{Dy}(\text{BTC})]_n$, by the solvothermal method, and study its catalytic activity and calcination at high temperatures for the synthesis of metal oxide.

EXPERIMENTAL SECTION

Apparatus and Reagents

Chemicals were purchased from Merck and Aldrich chemical companies. FT-IR spectra were recorded using Thermo Nicolet IR 100 FT-IR. The thermal behavior was measured with a PL-STA 1500 apparatus with the rate of $10\text{ }^\circ\text{C min}^{-1}$ in a static atmosphere of argon. The X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromated $\text{Cu-K}\alpha$ radiation. The samples were characterized by field emission scanning electron microscopy (FE-SEM) KYKY-EM 3200 with gold coating.

Preparation of Dy-MOF

A mixture of $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.5 mmol), benzene-1,3,5- tricarboxylic acid (0.25 mmol), DMF (4 mL), and H_2O (4 mL) was sealed in a 20

mL of Teflon-lined reactor. The pure colorless needle crystals of $\text{Dy}(\text{BTC})(\text{H}_2\text{O}) \cdot (\text{DMF})_{1.1}$ with yield of 62% were obtained after 24 h of heating at $105\text{ }^\circ\text{C}$. Anal. Calcd for $\text{Dy}(\text{C}_9\text{H}_3\text{O}_6)(\text{H}_2\text{O})(\text{C}_3\text{H}_6\text{ON})_{1.1}$: C, 31.64; H, 2.51; N, 3.30. Found: C, 31.21; H, 2.57; N, 3.35. IR (cm^{-1}): 1612 m, 1570 w, 1532 w, 1433 m, 1375 s, 1102 w, 942 w, 775 s, 710 m, 698 vs. 655 m, 560 s, 455 s, 433 m, 416 w.

For the purpose of activation, according to the TGA pattern analysis, when the Dy-MOF was heated to $330\text{ }^\circ\text{C}$ for 4 h, the coordinating solvent molecules began to be removed, and the compound retained its stability up to temperatures of $450\text{ }^\circ\text{C}$. Anal. Calcd for $\text{Dy}(\text{BTC})$: C, 29.25; H, 0.82. Found: C, 29.24; H, 0.85. IR (cm^{-1}): 1612 m, 1570 w, 1533 w, 1433 m, 1375 s, 1102 w, 942 w, 775 s, 710 m, 698 vs. 655 m, 560 s, 455 s, 434 m, 416 w.

Catalytic activity of Dy-MOF

In a typical experiment, a mixture of 1 mmol of diphenyl sulfide, 1.5 mmol of hydrogen peroxide along with an appropriate amount of Dy-MOF as catalyst (20 mg) was added to a flask containing a magnetic stirring bar in 1.5 ml ethanol at $30\text{ }^\circ\text{C}$ while the progress of the reaction was successfully followed by thin-layer chromatography (TLC) until all sulfides were consumed. Then the reaction was scaled-up and the resulting mixture was extracted with methylene chloride (10 mL x 2). The combined organic layers were washed with a saturated aqueous solution of sodium bicarbonate (15 mL) and dried over anhydrous magnesium sulfate and filtered. Evaporation of the filtrate afforded sulfoxide as colorless to pale yellow solids, which were purified by crystallization from EtOH to afford the desired product. The reactions were run out at least three times and the found values were averaged. All products are known compounds and were characterized by comparison of their physical and spectral data with those of authentic samples.

Synthesis of Dy_2O_3 particles

To prepare dysprosium (III) oxide particles, Dy-MOF prepared under solvothermal condition was calcined at $650\text{ }^\circ\text{C}$ for 5 h. After gradual cooling of samples, white precipitates of dysprosium (III) oxide particles were obtained and were characterized as final product. SEM images of these particles show a size distribution in the range of 80–200 nm.

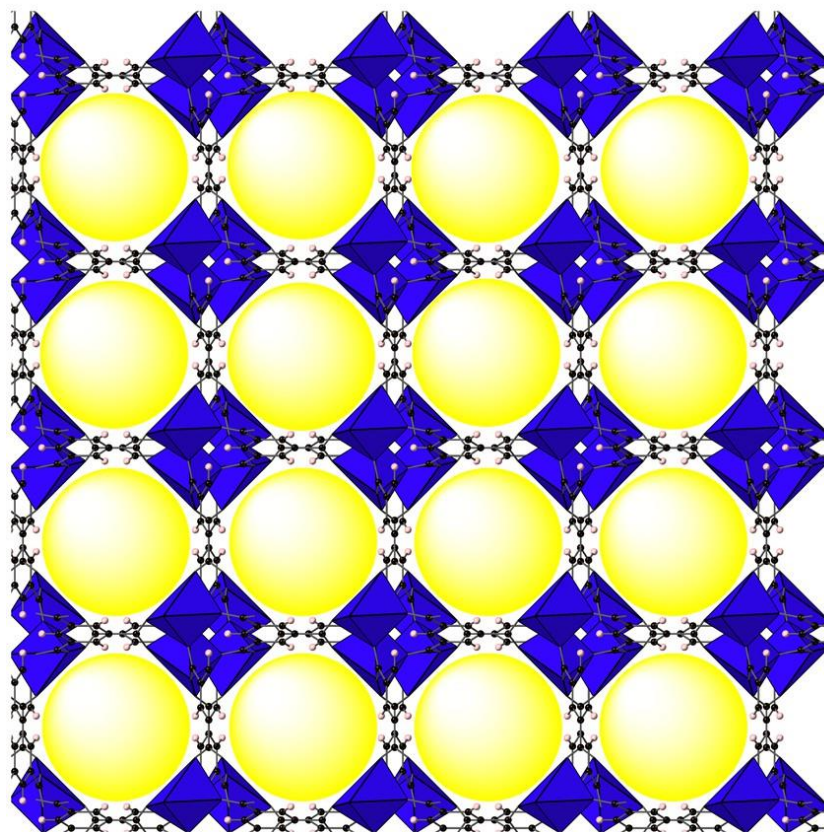


Fig. 1. Representation of the pores of dysprosium metal-organic framework

RESULTS AND DISCUSSION

Synthesis and characterization

The dysprosium-organic framework was prepared according to the procedure described by Xu and his coworkers [24]. reaction between dysprosium(III) nitrate hexahydrate and 1,3,5-benzenetricarboxylate (BTC) in mixed solvents of DMF and distilled water inside a Telon-lined autoclave at 105 °C for 24 h yielded Dy(BTC)(H₂O).(DMF)_{1,1}, which has been characterized by powder X-ray diffraction (PXRD), and FT-IR spectroscopy. The Dy(III) coordination environment can be considered as a distorted pentagonal-bipyramidal geometry around dysprosium formed by six oxygen atoms from six carboxylate groups of six BTC ligands and one oxygen atom from the terminal water molecule, Fig. 1. The open dysprosium sites are generated during the activation process (330 °C for 4 h) as result of the removal of coordinated water and *N,N*-dimethyl formamide molecules, trapped in pores, that remain after the MOF synthesis. The

activation of this framework was confirmed by FT-IR spectroscopy, elemental analysis, and powder X-ray diffraction (PXRD) analysis, Fig. 2. Also, the BET surface area of the activated Dy-MOF is determined to 690 m²/g, which is comparable to the reported surface area [24]. The high thermal stability, accessible open metal sites and nano-sized aperture for the Dy-MOF could endow it with a very high potential in different applications. The morphology and size of Dy-MOF prepared by the solvothermal method were characterized by field emission scanning electron microscopy (FE-SEM), Fig. 3.

Catalytic activity

Lanthanide coordination compounds are fascinating Lewis acids catalysts in organic synthesis. Their labile Ln-O_{DMF/water} bonds favor ready dissociation of substrates, allowing catalysis with high turnovers. To determine the general scope of sulfide oxidation, three substrates, namely dimethyl sulfide, methylphenyl sulfide,

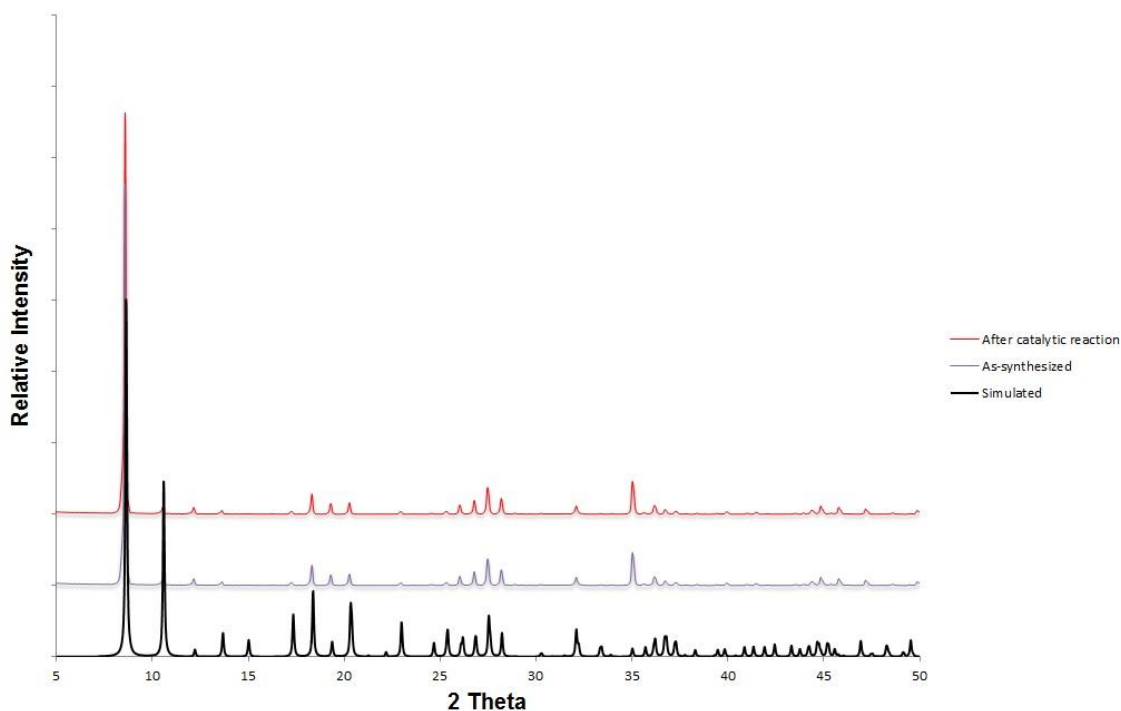
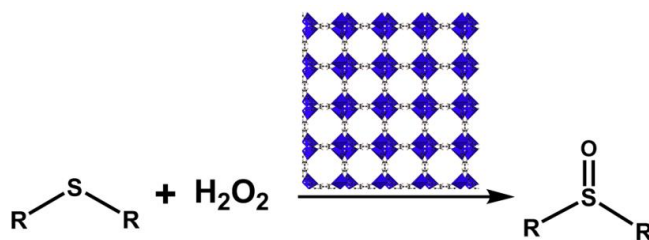


Fig. 2. PXRD patterns of simulated, as-synthesized, and after catalytic reaction of Dy-MOF

Table 1. The Dy-MOF-catalyzed sulfoxidation



Entry	Substrate	Product	Conversion and Yield (%) of sulfoxide formation	Reaction Time (min)	Product melting point (°C)
1	dimethyl sulfide	dimethyl sulfoxide	93	180	190-192
2	methylphenyl sulfide	methylphenyl sulfoxide	86	180	30-32
3	diphenyl sulfide	diphenyl sulfoxide	67	180	70-72

The catalytic reactions were run out at room temperature

and diphenyl sulfide were chosen and tested under optimized conditions. According to the section 2.3, in a typical experiment, a mixture of 1 mmol of sulfide, 1.5 mmol of hydrogen peroxide along with an appropriate amount of Dy-MOF as catalyst (20 mg) was added to a flask containing a magnetic stirring bar in 1.5 ml ethanol at room temperature

while the progress of the reaction was successfully followed by thin-layer chromatography (TLC) until all sulfides were consumed. Under this catalytic reaction condition, the selected sulfides are quantitatively converted to the sulfoxides by oxidation, with no observed sulfone. Table 1. However, in the absence of Dy-MOF, a limited

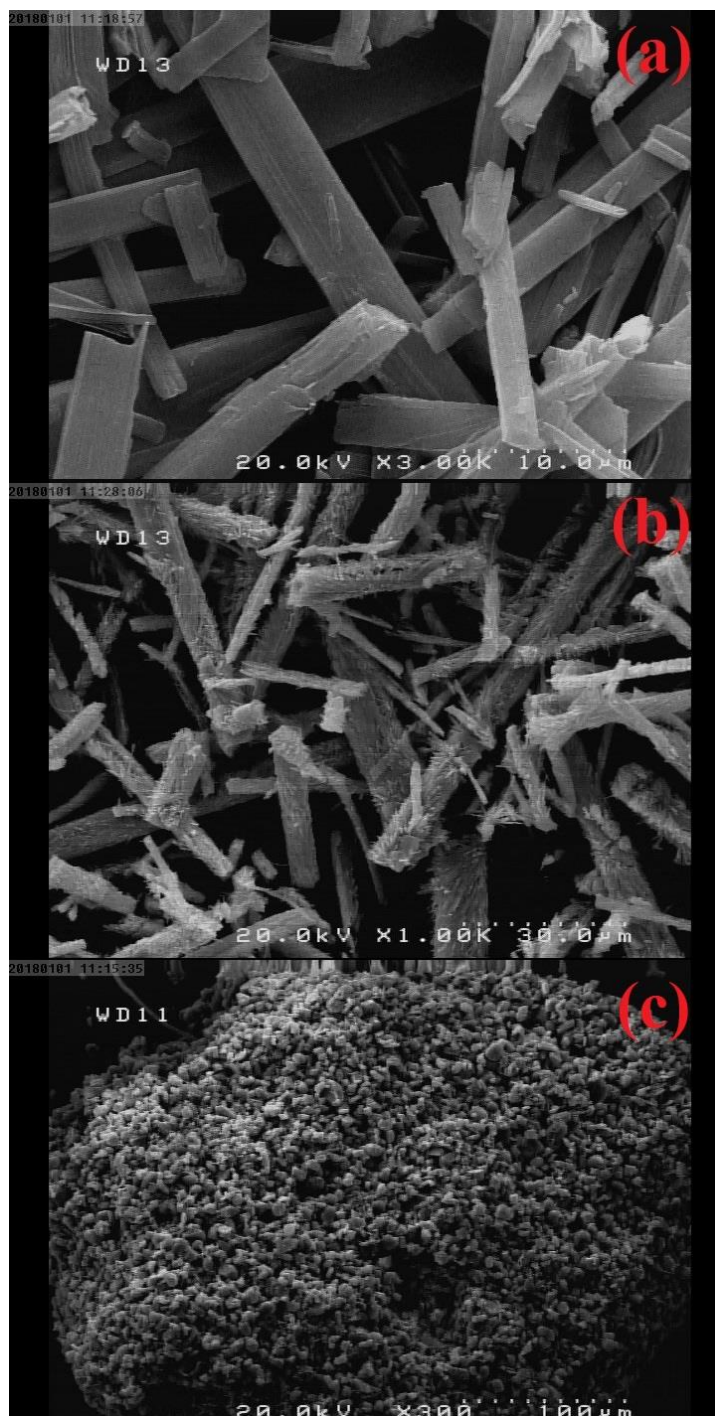


Fig. 3. SEM images of the as-synthesized (a) and after the catalytic reaction (b) of Dy-MOF particles and Dy₂O₃ particles (c).

sulfoxidation occurred very slowly to a maximum extent of 30 wt% on the basis of sulfide even in a longer time (10 h) of reaction. The PXRD pattern of Dy-MOF indicates that the framework remains intact after the catalytic reaction, as

supported by the good agreement between the FT-IR measurements before and after the reaction and scanning electron microscopy images, which is necessary for performing the reaction in the presence of a heterogeneous catalyst, Figs. 2 and 3.

Calcination and synthesis of dysprosium oxide

Particles of dysprosium oxide (Dy_2O_3) are also obtained by calcination of the $\text{Dy}(\text{BTC})(\text{H}_2\text{O})_n(\text{DMF})_{11}$ compound. The solvothermal synthesized block-shape particles were annealed at 650 °C for 5 hours in atmosphere. The crystal phase and the morphology of the resulting residue were qualitatively determined using PXRD and SEM, respectively. The observed characteristic reflections on 2θ of 20, 29, 33, 43, 48, and 57 in the resulting pattern are in a good match with the standard pattern of cubic Dy_2O_3 , space groups $Ia\bar{3}$ (206) with the lattice parameters $a = b = c = 10.6670 \text{ \AA}$ and $Z = 16$ (JCPDS card file No. 00-009-0197). Fig. 3 shows the morphologies of the Dy_2O_3 particles. While particles were formed by calcination of single crystal Dy-MOF, using rod-like Dy-MOF as a precursor leads to the dysprosium oxide particles.

CONCLUSION

In summary, herein, Dy-MOF with high chemical and thermal stability was successfully prepared by the reported procedure and was used as heterogeneous catalyst for sulfoxidation reaction and as precursor for the formation of nano- to micro-scale Dy_2O_3 particles. The framework has the active metal sites at Dy(III) centers, thus providing an accessible Lewis acid centers for the electrophile activation and as a result the sulfoxidation reaction occurs with the proposed mechanism where the active species of the oxidation reaction is the peroxy species. The results show that Dy-MOF can catalyze the sulfide oxidation reaction almost quantitatively to sulfoxide. Also, the crystals of Dy-MOF turn into nano- to micro-scale particles of Dy_2O_3 when heated at 650 °C in the air. This result suggests an approach for the formation of dysprosium oxide that has a well-defined (uniform) morphology.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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