

MOFs that catalyze air-based oxidations.

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Introduction

Coordination networks have gained increasing attention because of their potential applications in gas storage, sensor, separation, and catalysis.¹⁻² However, only a few catalytically active coordination polymers have been reported.³⁻⁶ The major obstacle in developing catalytic coordination networks is having the catalytically active center accessible to the substrate. In most of the coordination polymers, transition-metal-center potential catalytic sites are coordinatively saturated. Only very recently coordination polymers with catalytically active centers in the wall of the framework structures³⁻⁵ were reported. However, the catalytic sites in these materials are basic organic functional groups such as pyridine or acetate. There is only one example of a catalyst for hydrogen peroxide-based epoxidation.⁴ Given that oxidation catalysts are the most widely used in industry,⁷ developing coordination networks with such activities especially those that work with environmentally benign oxidants such as dioxygen or hydrogen peroxide are highly promising.

Materials and Methods

All chemicals, except 4-(chloromethyl)benzoic acid purchased from Alfa Aesar, were obtained from Aldrich. Dimethylacetamide (DMA) was dried with 3 Å molecular sieves prior to use. Other chemicals were used as received. Nicolet 510 FT-IR, Hewlett-Packard 8452A UV/Vis spectrophotometer, ISI TGA 1000, and ISI DSC 100 instruments were used to collect the corresponding data. Powder X-ray diffraction data were obtained by Ashland Specialty Chemical Co. General area detector diffraction system (GADDS) in a single crystal diffractometer is used for the routine qualitative evaluation of the crystallinity of the materials. Oxidation reactions were quantified by Hewlett Packard 6890 series gas chromatograph. The triol derivative, (4-HOOC₆H₄)CH₂NHC(CH₂OH)₃ (Acid-Tris), was prepared by the reaction of tris(hydroxymethyl)aminomethane, (HOCH₂)₃CNH₂ (35.6 g, 0.294 mol), and 4-chloromethylbenzoic acid, (4-HOOC₆H₄)CH₂Cl (10.0 g, 0.0586 mol), in water (300 mL) at 22°C for 20h. The bis(benzoic acid)-capped hexavanadate, [(*n*-C₄H₉)₄N]₂[V₆O₁₃((CH₂O)₃CN HCH₂(4-C₆H₄COOH)₂] (TBA₂[H₂I]), was prepared by the reaction of Acid-Tris with [(*n*-C₄H₉)₄N]₃[H₃V₁₀O₂₈]⁸ in DMA at 85 °C for 24h under O₂.⁹ General preparation of LnI materials (Ln = Gd^{III}, Tb^{III}, or Yb^{III}). To a TBA₂[H₂I] solution (10 mM, 10 mL) in DMF, a Ln(NO₃)₃ (Ln = Gd^{III}, Tb^{III}, or Yb^{III}) solution in DMF (20 mM, 5.5 mL) was added. The solution was stirred for 5 min, and then 0.8 mL of MeOH was added. The solution was allowed to stand undisturbed for 2-5 days. Red crystals were filtered and washed with MeOH and then air-dried for 2 days to afford 130-140 mg of product (70-80 % yield).

Results and Discussion

In LnI (Ln = Gd or Tb), each lanthanide ion(III) is eight coordinate with a square antiprismatic geometry with 4 oxygen atoms from 4 benzoic acid moieties of **1** on one square and 4 oxygen atoms from solvent molecules (3 DMF molecules and 1 water molecule) on the other square. Two lanthanide atoms are connected by 4 benzoic acid-moieties of **1** to form a

paddle-wheel cluster. The paddle-wheel cluster units are extended by **1** to form two dimensional (2D) coordination layers. The 2D layers are further connected by hydrogen bonds between one of the two secondary amines and a bridging oxo group of the POM. Microporous channels are formed along the crystallographic a and c axes. The stacking mode of the 2D layers is ABCABC... style, which resembles a cubic closed packed arrangement. As a result, the dimensions of the channels are much smaller than that of the cyclic tetrameric linkage formed by the paddle-wheel clusters and **1** (Figure 1).

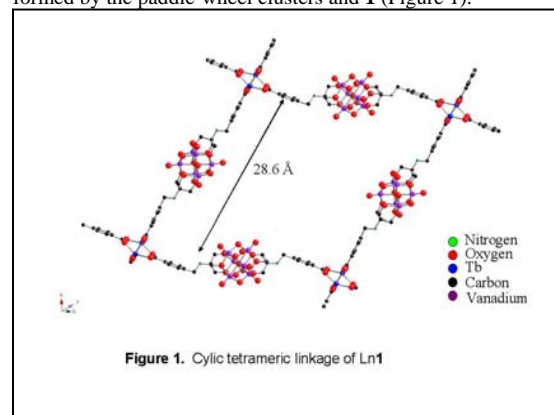


Figure 1. Cyclic tetrameric linkage of LnI

The catalytic activity of YbI was evaluated in dichloroethane, a solvent in which the coordination polymer is totally insoluble. YbI catalyzes the aerobic oxidation of PrSH to its corresponding disulfide product, PrSSPr, at 45 °C (7.8% conversion, three turnovers, based on the molar equivalents of V₆ groups in YbI present, after a reaction period of 70h). In the absence of the catalytic microporous coordination polymer, no

PrSSPr was produced (the limit of detectability is <0.1% conversion). The supernatant showed no catalytic activity; whereas, the recycled catalyst maintained catalytic activity. Powder XRD confirms that recovered YbI retains crystallinity after reaction.

Significance

MOF-like materials that catalyze potentially useful air-based oxidations have been realized.

References

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