Utilizing mixed-linker zirconium based metal-organic frameworks to enhance the visible light photocatalytic oxidation of alcohol

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HIGHLIGHTS

- We synthesize mixed-linker Zr-MOFs catalyst in one pot.
- Mixed-linker MOFs are characterized by PXRD, NMR, DRIFTS, STEM and N_2 sorption.
- Mixed-linker MOFs show significant enhancement in visible light photocatalysis.
- Mixed-linker MOFs selectively oxidize benzyl alcohol to benzaldehyde.

GRAPHICAL ABSTRACT
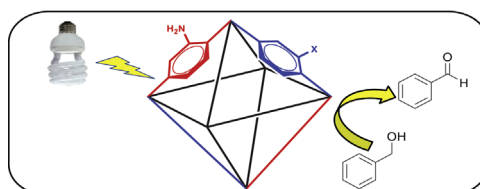
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ABSTRACT

A series of mixed-linker zirconium-based metal-organic frameworks (Zr-MOFs) have been synthesized in one-pot reactions. The Zr-MOFs, containing 2-amino-1,4-benzenedicarboxylate (NH_2-BDC) as the primary linker and 2-X-1,4-bezenedicarboxylate (X-BDC, X=H, F, Cl, Br) as a secondary linker, have been used as visible light photocatalysts. The incorporation of multi-functional groups into the catalysts was characterized by PXRD, STEM, NMR, N_2 physisorption, diffuse reflectance FTIR, and diffuse reflectance UV–vis. The effects of different linkers on the photocatalytic property of the Zr-MOFs were evaluated in the oxidation of benzyl alcohol. The photocatalytic oxidation reaction was performed using a 26 W helical bulb as the visible light source, and the temperature of the reaction was kept at 80 °C. The Zr-MOF containing mixed NH_2-BDC and F-BDC linkers gives five times more conversion in the oxidation of benzyl alcohol compared to the Zr-MOF made of mixed NH_2-BDC and H-BDC linkers. We only observed partial oxidation product, benzaldehyde, from the photocatalytic oxidation reaction.

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1. Introduction

Since the discovery of ultraviolet (UV) light-irradiated, photocatalytically active TiO_2 by Fujishima and Honda (1972), immense efforts have been directed to improve the efficiency of this semiconductor (Linsebigler et al., 1995). This led to a spurt of research towards utilizing light as an effective source of energy for many important chemical transformations. By applying molecular orbital theory, significant advances have been made in the design of these photocatalysts owing to an improved understanding of the utilization of light energy by molecules (Duncan and Prezhdo, 2007). Traditional semiconductors, quantum dots (Kamat, 2008), and supramolecular ensembles (Peng et al., 2012) have also been engineered to efficiently execute photocatalytic reactions. A new class of materials, a hybridized organic–inorganic structural motif known as metal-organic framework (MOF) has emerged as an interesting multi-purpose platform. MOFs have found considerable applications in gas storage

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(Suh et al., 2011), heterogeneous catalysis (Kuo et al., 2012; Gascon et al., 2013), separations (Li et al., 2009), drug delivery (Zhuang et al., 2014), and chemical sensing (Kreno et al., 2011). Interestingly, due to the inherent ability to control the functionality of the organic linkers and the inorganic secondary building units during their synthesis (Eddaoudi et al., 2002), these materials have shown considerable promise for photocatalysis.

Application of MOFs in photocatalysis was first rationalized in the MOF-5 system due to its semiconductivity (Alvaro et al., 2007; Gascon et al., 2008). However, MOF-5 is only active as a catalytic system upon UV light irradiation. To tune the band gap of MOFs to absorb visible light, Fu et al. (2012) and other groups (Long et al., 2012; Nasalevich et al., 2013) modified the type of organic bridging linkers and produced visible light active catalysts. However, the catalytically active sites that reside at the inorganic building blocks of these MOFs yield relatively low activity (Nasalevich et al., 2014). In comparison, MOF-based photocatalysts synthesized by Lin et al. (2011) through linker coordination with redox metal complexes show significantly enhanced photocatalytic activity in water oxidation, CO_2 reduction, and organic transformations (Wang et al., 2011).

We hypothesized that incorporating different linkers of appropriate functionalities into a single framework could affect its catalytic property which provides a new opportunity for designing improved catalysts. In literature, the incorporation of different functionalized linkers into a single MOF has been demonstrated by Burrows and coworkers through post-synthetic modification (PSM) (Burrows et al., 2008). Starting with aldehyde-functionalized MOF-5, comprised of ZnO_4 clusters connected by aldehyde-functionalized benzenedicarboxylate linkers, Burrows intended to chemically modify the aldehyde group to other useful groups. However, the aldehyde group was only modified partially, resulting in a mixed-linker MOF system. Using a bottom-up approach, Deng et al. (2010) incorporated up to six linkers with different functional groups into MOF-5. This MOF was synthesized by a one-pot synthesis approach, where the different linkers were added at the beginning of the synthesis. Besides MOF-5 system, Marx et al. (2010) introduced mixed linkers into MIL-53(Al). Taylor-Pashow et al. (2009) produced mixed-linker MIL-101(Fe) for drug delivery applications.

In this report, we synthesized task-specific mixed linker Zr-MOFs using bottom-up approach in one-pot, aiming to improved activity in visible light photocatalytic reactions. We utilized 2-amino-1,4-benzenedicarboxylic acid (NH_2-BDC) as a primary linker to shift the absorption wavelength of the parent UiO-66 which comprise of of $Zr_6O_4(OH)_4$ clusters and 1,4-benzenedicarboxylate (BDC) linker (Cavka et al., 2008) to the visible light regime, and a secondary linker, 2-X-1,4-benzenedicarboxylic acid (X-BDC, where X=H, F, Cl, Br) was incorporated in the same MOF to adjust the local environment and electronic properties around the active sites and thus their activity. Their catalytic performance was evaluated in the visible light photocatalytic oxidation of benzyl alcohol. The as-synthesized mixed-linker UiO-66 MOFs containing halogen functional groups showed enhanced catalytic activity compared to the UiO-66–NH_2 and UiO-66–NH_2–H MOFs.

2. Experimental

2.1. Catalyst preparation

Anhydrous zirconium tetrachloride ($ZrCl_4$, 98%), and 2-amino-1,4-benzenedicarboxylic acid were purchased from Acros Organics. 2-bromo-1,4-benzendicarboxylic acid and was purchased from Alfa Aesar and benzenedicarboxylic acid was purchased from Sigma Aldrich. All chemicals were used without further purification. 2-chloro-1,4-benzendicarboxylic, 2-fluoro-1,4-benzenedicarboxylic acid, and 2-iodo-1,4-benzenedicarboxylic acid were synthesized according to a reported procedure in literature (Vermoortele et al., 2012; Meek et al., 2011).

For the synthesis of 2-iodo-1,4-benzenedicarboxylic acid and 2-fluoro-1,4-benzenedicarboxylic acid, the respective functionalized dimethyl terephthalate was used. In general, 0.5 g (2.36 mmol) of dimethyl-2-fluoroterephthalate was dissolved in 20 mL of aqueous sodium hydroxide (NaOH, 1.0 M) at 353 K for 30 min with continuous stirring. After 30 min, the clear solution was cooled down to room temperature. Concentrated hydrochloric acid (HCl, assay 37%) were added dropwise to the solution while stirring until the pH reaches 1. The resultant white precipitate was recovered by vacuum filtration, and wash with copious amount of water to remove the excess acid. The white powder was vacuum dried overnight at room temperature.
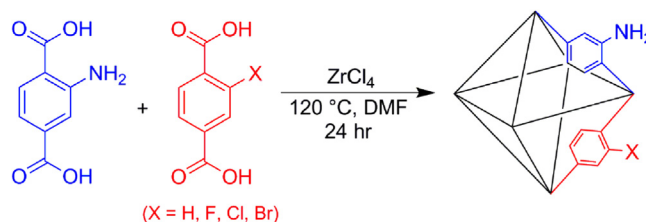
For the synthesis of 2-chloro-1,4-benzenedicarboxylic acid, 0.5 g (3.25 mmol) of 3-chloro-4-methylbenzoic acid and 1.6 g (9.8 mmol) of potassium permanganate were dissolved in 20 mL aqueous potassium hydroxide solution (KOH, 2 M). The solution was set to refluxed overnight. The solution was allowed to cool to room temperature and acidified with concentrated hydrochloric acid to pH 1. The precipitate was collected by vacuum filtration and rinse with copious amount of water. The precipitate was dried in vacuum at room temperature to obtained 2-chloro-1,4-benzenedicarboxylic acid.

UiO-66–NH_2 was synthesized according to a process reported in literature (Guo et al., 2014). In a typical synthesis, 1.7 mmol of zirconium tetrachloride ($ZrCl_4$) was dissolved in 100 mL of dimethylformamide (DMF) in a Teflon PFA wide mouth jar. An equimolar amount of the linker, 2-amino-1,4-benzenedicarboxylic acid (1.7 mmol), was dissolved into the clear solution with the aid of sonication for about 5 min. The tightly capped Teflon jar was then transferred into a 120 °C pre-heated oven. The Teflon jar was maintained under static conditions for 24 h. After 24 h, the suspension was cooled to room temperature and the precipitate was isolated by centrifugation at 8000 rpm for 15 min. The isolated precipitate was washed with 40 mL of DMF thrice to remove any unreacted substrates. The precipitate was further washed with methanol to allow the exchange of DMF trapped in the framework with a lower boiling point solvent. During each wash, the suspension was kept at room temperature for 12 h before being centrifuged. Finally, the precipitate was dried at 150 °C under dynamic vacuum overnight to remove the trapped solvent.

For the synthesis of mixed-linker Zr-MOFs (Scheme 1), 1.7 mmol of zirconium tetrachloride was dissolved in 100 mL of DMF in a Teflon PFA wide mouth jar. The primary linker 2-amino-1,4-benzenedicarboxylic acid (0.85 mmol) and the second organic linker 2-X-1,4-benzendicarboxylic acid (0.85 mmol, X=H, F, Cl, Br) were dissolved into the solution by sonication. The Teflon jar was sealed and transferred into a 120 °C preheated oven. After 24 h, the precipitate was isolated, purified and dried following the same procedure used for UiO-66–NH_2. The as-synthesized mixed-linker UiO-66 MOFs were denoted as UiO-66–NH_2–X (X=H, F, Cl, Br).

2.2. Catalyst characterization

The powder X-ray diffraction (PXRD) patterns were collected at room temperature using a STOE Stadi P powder diffractometer

Scheme 1. Synthesis of the mixed-linker Zr-MOFs. Equimolar quantities of primary linker 2-amino-1,4-benzenedicarboxylic acid and secondary linker 2-X-1,4-benzenedicarboxylic acid (X=H, F, Cl, Br) .