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MOF-808 as a recyclable catalyst for the photothermal acetalization of aromatic aldehydes



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ABSTRACT

Metal-organic frameworks (MOFs) show promise for catalysis applications due to their porosity, high internal surface area, and structural adaptability. Typical acetalization reactions of aldehydes require elevated temperatures and excess alcohol to drive the reactions to completion. In this current work, MOF-808 is used as a heterogeneous catalyst for acetylation of aldehydes in methanol using a mild photothermal process. Optimized conditions gave 72% yield of 2-(dimethoxymethyl)naphthalene in the presence of 10 mol% MOF-808 at 45 °C using only a fluorescent lamp. MOF-808 can be recycled up to 5 times with no loss in catalytic activity. A proof-of-principle substrate scope demonstrates the potential utility for aromatic and aliphatic substrates.

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adaptability including gas storage and gas separation [17,18], toxic chemical and heavy metal remediation [19,20], drug delivery [21], and heterogeneous catalysis [22,23]. MOFs have been used as solid acid catalysts for epoxide ring opening, cycloadditions (including the Diels-Alder reaction), Knoevenagel condensations, redox reactions, photocatalytic reactions, and even polymerization [24]. Oftentimes these reactions are catalyzed by the secondary building unit (SBU) that piece the frameworks together, providing in some cases accessible unsaturated Lewis acid sites [25,26]. It is therefore unsurprising that MOFs have previously been studied as catalysts for acetalization of aldehydes and ketones [27,28].

MOF-808, $Zr_6O_4(OH)_4(C_9H_6O_6)_2(HCO_2)_6$, is a relatively robust 3D network with two pores measuring 4.8 Å and 18.4 Å internal pore diameter [29]. The SBU connects to six 1,3,5-benzenetricarboxylic acid (BTC) linkers leaving six empty sites for formate anions to coordinate. These μ_2 anionic ligands can be exchanged for μ_1 oxy ligands, leaving coordinatively-unsaturated Lewis acidic sites for catalysis [30]. Despite the ease of preparation and stability of MOF-808, it has not previously been used as a catalyst for acetalization of aldehydes (notably a Ru@MOF-808 catalyst has been found to promote the sequential oxidation/acetalization of aliphatic alcohols, while the authors found only formation of hemi-acetal using MOF-808) [31]. Considering that the SBU of MOF-808 can promote Meerwein–Ponndorf–Verley reduction [32], hydrogenation of furfural to furfuryl alcohol [33], and catalytic dehydration of tertbutyl alcohol [34], we reasoned that it should be capable of

1. Introduction

Conversion of aldehydes into protected acetals is essential in synthetic organic [1], medicinal [2,3], and carbohydrate [4,5] chemistry to achieve chemoselective product formation. Acetals are also valuable additives for a variety of material and fuel applications [6–8]. The synthesis of acetals from aldehydes and ketones typically requires treatment of the carbonyl substrate with an alcohol in the presence of an acid catalyst. This transformation is generally promoted through the use of homogeneous protic [2,9] or Lewis acid [10,11] catalysts, and due to its reversibility, the water by-product must be driven off or an excess of alcohol used. Alternatively, molecular sieves/zeolites [12,13] as well as other porous compounds can facilitate acetal formation when they contain acidic functionality, while porous structures can aide in the removal of water from the reaction to drive the equilibrium towards acetal production.

Metal-organic frameworks (MOFs) are a class of materials known for their robust porosity, high surface area, and crystallinity [14]. Unlike zeolites, the use of organic linkers in MOFs allows their properties to be easily tuned [15,16]. MOFs therefore have a wide range of applications thanks to their atomic and molecular

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promoting acetalization as well.

2. Results and discussion

MOF-808 was synthesized according to a known solvothermal procedure [35], and was confirmed by comparison of the powder xray diffraction and FTIR data with literature data. While many acetalization catalysts operate under thermal conditions, we were interested in recent work using thiourea catalysts for acetalization that are activated by light at room temperature [36]. The pK_a of the photo excited state was found to be lower, thereby increasing the rate of acid catalysis. Considering the potential of MOF-808 to absorb light ($\lambda_{max} = \sim 254$, 292 nm when suspended in MeOH), we considered that photoactivation with light could provide similar access to increased acidity for acid-based catalysis. We therefore began investigating the activity of MOF-808 for the acetylation of aldehydes under mild photolytic conditions (Table 1) using 2naphthaldehyde (1a) as a model substrate in methanol to prepare the dimethyl acetal 2a. While GC-MS is a common analytical technique used to analyze product yield, we found that analyzing samples directly in the alcohol solvent gave some conversion to acetal product, and so the yield and conversion was instead determined by ¹H NMR using an internal standard after a simple work-up procedure.

Gratifyingly, we were able to find that by simply placing our samples on a stir plate between two 26W fluorescent work lamps overnight, the reaction could be achieved with 90% conversion and 72% yield as determined by NMR (Table 1, **Entry 1**). Under the reaction conditions, the temperature was found to stabilize at 45 °C, which suggested that perhaps the reaction was thermal in nature. However, in the absence of light the conversion and yield were both lower (**Entry 2**), suggesting an important role for light. To ensure

Table 1

Optimization of the photothermal acetalization of 2-naphthaldehyde with Methanol.



| Entry | Reaction Conditions | Conversion (%) | Yield (%) |
|-------|----------------------------------|----------------|-----------|
| 1 | Standard Conditions ^a | 90 | 72 |
| 2 | Absence of Light | 85 | 58 |
| 3 | Absence of Heat | 54 | 30 |
| 4 | Absence of Light RT | 49 | 15 |
| 5 | Natural Light RT | 55 | 36 |
| 6 | Absence of MOF-808 | 7 | 7 |
| 7 | ZrCl ₄ as Cat. | 17 | 0 |
| 8 | Trimesic Acid as Cat. | 13 | 0 |
| 9 | 20 mol% MOF-808 | 77 | 29 |
| 10 | 30 mol% MOF-808 | 80 | 28 |
| 11 | 40 mol% MOF-808 | 82 | 10 |
| 12 | 50 mol% MOF-808 | 80 | 15 |
| | | | |

^a "Standard Conditions": A 7.5 mL vial was charged with 2-naphthaldehyde (0.1 mmol, 15.6 mg), MOF-808 (0.01 mmol, 10 mol%, 13.5 mg), and MeOH (1 mL). The vial was sealed with a PTFE-lined cap and stirred under two 26-W twin-tube fluorescent work lights at 45 °C [37]. After cooling to room temperature, the MeOH was evaporated and replaced with CDCl₃ and a drop of dibromomethane (DBM) standard added.

the reaction was actually at the expected temperature and not a bit higher, we ensured the temperature had stabilized using a thermometer in an oil bath prior to setting-up the reactions. We next performed the reaction, but ensured sufficient air circulation to keep the system at room temperature (**Entry 3**), which still gave 30% yield of the product (also monitored using a thermometer and oil bath). To compare these results to the background reaction, we next looked at the effect of running the reaction at room temperature, but keeping the flask in the dark (**Entry 4**), in which case a lower 15% yield was observed. By leaving the reactions on a windowsill exposed to ambient sunlight (but at room temperature, **Entry 5**) we found comparable yields to running the reactions under the lamps at room temperature.

When the MOF was excluded, only 7% yield of acetal was found under the photothermal conditions (Entry 6). To ensure the MOF was directly involved as opposed to possible degradation products, we next screened ZrCl₄ (Entry 7) and the ligand trimesic acid (Entry 8). Notably, in the case of ZrCl₄ we expect the identity of the active catalyst to more accurately reflect the degradation products of the MOF after solvolysis, rather than actually being ZrCl₄ [38]. In both cases no desired product was observed, suggesting that the activity is specific to the MOF, and that the individual components even slow the background reaction. We next studied how the catalyst loading impacted the conversion. We had assumed that increasing the amount of framework would increase the conversion - however, the reaction appears to be hindered by additional catalyst (Entries 9-12). We noticed from direct analysis of the crude reaction by GC-MS that when the conversion was high but vield was low, sometimes significant amounts of additional side products were observed, including benzyl alcohol and methyl benzoate. Notably, the catalyst loading was based on the molecular weight for $[Zr_6O_4(\mu_3-OH)_4(FA)_6(BTC)_2]$, which will be slightly undervalued since it ignores the undefined amount of residual solvent that will be filling the pores.

We next explored the reaction on different substrates (Fig. 1). 2-Naphthaladehyde worked well to give 2a, while 1-naphthaldehyde gave a lower yield of **2b**. Benzaldehyde worked relatively well based on TLC and GC-MS analysis of the crude reaction (2c), however, the volatility of the product caused the average yields to be lower. Larger 9-anthracene carboxaldehyde as well as 1-pyrene carboxaldehyde could be converted to 2d and 2e respectively, although the conversion and therefore yield were lower. The sterically-hindered o-tolualdehyde was not very effectively converted into 2f during the reaction, but the less sterically-hindered *m*- and *p*-tolualdehydes gave the acetal products **2g** and **2h** in much better yields. We reasoned that salicylaldehyde might be a better substrate despite sterics thanks to intramolecular hydrogen bonding, but the acetal 2i was recovered in relatively low yield. Surprisingly, *p*-anisaldehyde also gave low yield of acetal 2j. Terephthaldehyde was a very effective substrate, giving full conversion and more importantly good selectivity for the diacetal 2k. Aliphatic aldehydes were not very efficiently converted (2l and 2m), while heterocyclic acetal 2n was not observed under the current conditions (only the 2-furfural starting material was recovered). Notably, when we investigated the crude reaction mixtures by NMR and GC-MS, we found the majority of the mass balance for these reactions were aldehyde and acetal, with trace amounts (<5%) of the corresponding esters and cinnamaldehydes. We also evaluated the reaction conditions for the acetalization of D-(+)-glucose, but not only was the α -methylglucoside not observed, partial dehydration of the glucose was observed to occur.

Because the system could promote formation of acetals in methanol, we next considered whether or not the reverse hydrolysis could be achieved by using water. MOF-808 is known to be relatively robust in water at elevated temperatures, so the reaction



Fig. 1. Substrate Scope of Dimethylacetalization of Aldehydes. All reactions performed on 0.1 mmol scale in triplicate, and the average yield reported. Yields were determined by ¹H NMR using dibromomethane as standard.

seemed possible. However, after subjecting benzaldehyde dimethyl acetal to the reaction conditions using water as the solvent, neither product nor starting material was recovered. Instead, the major observed product was determined to be benzoic acid, though in relatively low yield (<20%). Because of the open coordination sites on the framework, the low yield is most likely a result of benzoic acid binding in the framework.

Considering the heterogeneity of the catalyst, we expected that the system should be amenable to catalyst recycling. We therefore ran the reaction with the MOF, and then after isolation, washing, and drying, resubjected it to the reaction conditions (Fig. 2). The catalyst maintained its activity over five subsequent uses,



Fig. 2. Recyclability study of MOF-808 for the photothermal acetalization of 2-naphthaldehyde with methanol.

suggesting that this catalyst system might be well-suited to flow applications because of the stability of the MOF-808 framework. Notably, analysis of the framework by PXRD demonstrated no loss of crystallinity after each successive run. This increase in conversion/yield (overall recovery in general) after successive runs is commonly observed while using MOF-based catalysts [39–41]. We reasoned that this could be a result of starting material or product becoming trapped inside the pores and exiting on the next cycle. To this end we took a washed catalyst after the end of a run and digested it using NaOH in D₂O. In this case we saw only trimesic acid and a trace amount of formic acid (likely caused by degradation of the DMF solvent during the synthesis of the framework) [42]. However, extraction with CDCl₃ and subsequent NMR analysis showed that indeed some of the acetal product had been stuck in the framework.

3. Conclusions

We have demonstrated herein that using a combination of heat and light can be useful to drive the formation of acetals from aldehydes and methanol in the presence of MOF-808. The catalyst shows good stability and reusability for dimethyl acetal formation. While the role of light is somewhat unclear, we demonstrated through controls that it was clearly benefitting the reactions. We hypothesize that the improvement to the reaction can be increased by using a light source that is closer to the absorbance bands of MOF-808 below 300 nm. Further work on applications of photothermal reactions using MOF-808 are underway in our lab.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132036.

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