

Heterogeneous Catalysts

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An Efficient Iron(III)-Catalyzed Aerobic Oxidation of Aldehydes in Water for the Green Preparation of Carboxylic Acids

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Abstract: The first example of a heterogeneous iron(III)-catalyzed aerobic oxidation of aldehydes in water was developed. This method utilizes 1 atmosphere of oxygen as the sole oxidant, proceeds under extremely mild aqueous conditions, and covers a wide range of various functionalized aldehydes. Chromatography is generally not necessary for product purification. Its operational simplicity, gram-scale oxidation, and the ability to successively reuse the catalyst, make this new methodology environmentally benign and cost effective. The generality of this methodology gives it the potential to be used on an industrial scale.

Oxidation is one of the most fundamental reactions in nature with the oxidation of aldehydes to carboxylic acids being one of the most well-known and most frequently used methodologies.^[1] Although carboxylic acids are readily obtained in the laboratory by oxidation of the corresponding aldehydes, highly efficient and environmentally benign transformations of aldehydes into carboxylic acids still remain challenging.^[2] Even today, the majority of these oxidation reactions require stoichiometric amounts of hazardous oxidants such as KMnO_4 ,^[3] CrO_3 ,^[4] KHSO_5 ,^[5] KIO_4 ,^[6] etc., and often take place in harmful solvents (Figure 1a). Thus, environmentally benign oxidation protocols are greatly desired. Molecular oxygen possesses a number of advantages over other oxidants, and reactions that use molecular oxygen have a high atom economy and produce water as the only byproduct. However, catalytic oxidations of aldehydes into carboxylic acids with molecular oxygen as a terminal oxidant remain scarce. The limited number of catalysts available for the direct activation of molecular oxygen and the need for rare and expensive noble metals as catalysts restricts its use.^[7–10] Moreover, most of the systems reported so far require

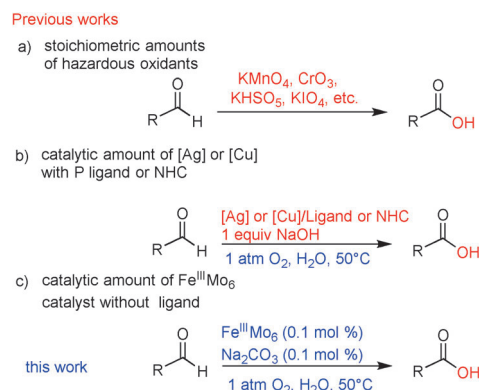


Figure 1. Oxidation of aldehydes into carboxylic acids.

the use of expensive metals, ligands that are not commercially available, and aerobic catalyst systems than cannot be recycled, thus leading to prohibitively expensive costs for practical application.^[11–13] Therefore, the use of inexpensive and earth-abundant transition-metal catalyst systems, which employ molecular oxygen as a terminal oxidant, are highly desired. The natural abundance of water and its inherently greener characteristics compared to common organic solvents, makes it extremely attractive for the development of more environmentally benign reactions.^[14] Recently, catalytic aerobic oxidation methodology has received a great deal of attention because of its high efficiency and operational simplicity. For example, Li et al.^[2] reported the first example of a homogeneous silver- or copper-catalyzed aerobic oxidation in water, successfully oxidizing various aldehydes into carboxylic acids with almost 100% conversion under mild reaction conditions (Figure 1b). Nevertheless, such methodologies are uncommon and the organic ligands employed in these reactions are susceptible to oxidative self-degradation and limits their usefulness.

Polyoxometalates (POMs),^[15] a large class of structurally well-defined anionic molecular metal-oxygen clusters with more-stable thermal and oxidative redox properties than organometallic complexes, have been used extensively as efficient catalysts in a number of oxidation reactions because of both their resistance towards oxidation and compatibility with various oxygen sources.^[16] In particular, POMs are commonly used as soluble molecular oxide supporters to assist metal ions for homogeneous catalysis. In this respect, Anderson-structured POMs^[17] are very important since they consist of a single metal atom supported by a polymolybdate or polytungstate. This polymolybdate or polytungstate is composed of six-edge sharing MO_6 ($M = \text{W}$ or Mo) octahedra surrounding a central, edge-sharing metal heteroatom octahedron (XO_6) with six protons.

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These protons or the corresponding hydroxy groups can be replaced with organic ligands to yield organic hybrid POMs. The ease with which the oxometal cluster can be modified allows the preparation of new POMs for potential applications in different research fields.^[18] However, to the best of our knowledge, their use as catalysts for the oxidation of aldehydes into carboxylic acids have, until now, not been reported. We herein describe a simple, mild, and efficient aerobic oxidation of aldehydes in water using an organic-hybrid POM catalyst, a single-sided triol-functionalized iron-centered Anderson polyoxometalate,^[19] $[[N(C_4H_9)_4]_3[FeMo_6O_{18}(OH)_3\{(OCH_2)_3CNH_2\}]]$ ($[Fe^{III}Mo_6]$ catalyst (**1**); Figure 2). The reaction can be conducted at a low pressure (1 atm) using molecular oxygen as the terminal oxidant (Figure 1c). The catalyst can be recycled and used in successive reactions without any degradation in catalyst performance.

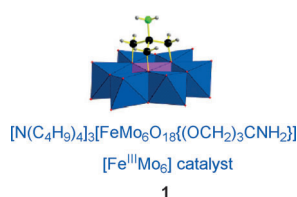


Figure 2. $[[N(C_4H_9)_4]_3[FeMo_6O_{18}(OH)_3\{(OCH_2)_3CNH_2\}]]$.

Catalytic studies began with the oxidation of benzaldehyde (1.5 mmol) with O₂ (1 atm) in the presence of **1** (0.1 mol %) under aqueous reaction conditions. The reaction was carried out at 50 °C using various additives (Table 1). We found the efficiency of the transformation to be strongly affected by the basicity of the additives (entries 1–18). When Na₂CO₃ (pK_b = 3.67) was added to the reaction system, benzoic acid was obtained in 95 % yield (entry 2), while the addition of NaHCO₃ (pK_b = 7.95) reduced the yield of benzoic acid to 63 %. (entry 3). Use of Na₂SO₃ (pK_b = 6.8) further decreased the yield to 26 % (entry 5) while Na₂SO₄ (pK_b = 12.0) providing the lowest yield of 5 % (entry 4). For the organic basic additives, such as CH₃COONa and Et₃N, gave benzoic acid in 83 and 89 % yields, respectively (entries 6 and 7). Additives with a neutral salt, such as NaBr, KCl, and NaCl, gave only moderate yields of the oxidized product (entries 7–9).

The acidic additive NH₄Cl severely inhibited the oxidation (Table 1, entry 11). These results show that the additive clearly influences the activity of the Fe^{III}Mo₆ polyoxometalate catalyst, probably because the acid-base properties of POMs are highly tunable. Furthermore, the impact of varying the catalyst loading and reaction temperature were investigated. Altering the catalyst loading had little influence on the product yield (entries 2, 12–14). With increasing reaction temperature, the yield of the benzoic acid product reached the maximum at a temperature of 50 °C (entries 12, 15, and 16). Further raising the reaction temperature to 70 °C lowered the yield to 96 % (entry 18), possibly because of the reduced contact between the O₂ (in the gas phase) and the catalyst. Switching from oxygen gas to air and using the same

Table 1: Optimization of reaction conditions.^[a]

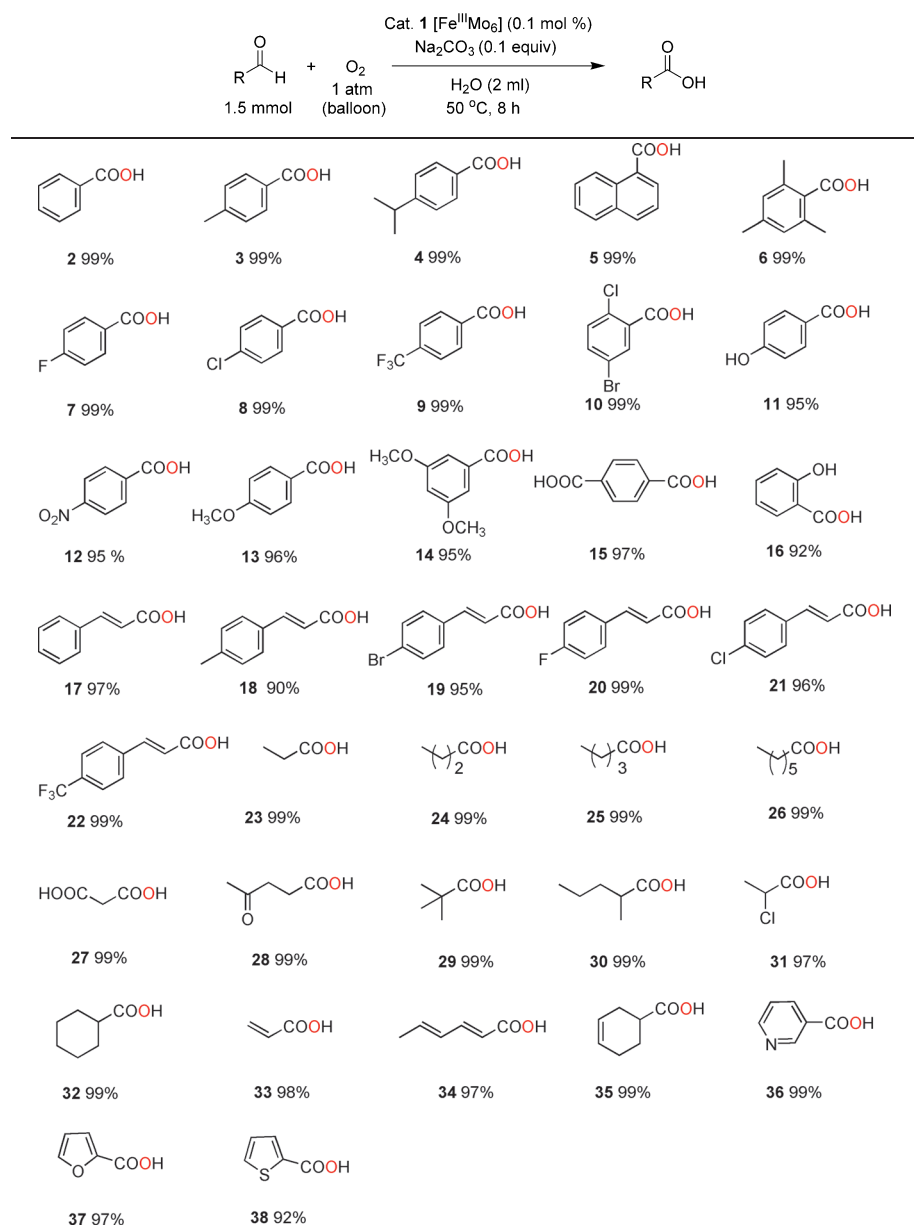
Entry	Additive	Mol% cat.	T [°C]	Yield [%] ^[b]
1	–	0.5	50	35
2	Na ₂ CO ₃	0.5	50	95
3	NaHCO ₃	0.5	50	63
4	Na ₂ SO ₄	0.5	50	5
5	Na ₂ SO ₃	0.5	50	26
6	CH ₃ COONa	0.5	50	83
7	Et ₃ N	0.5	50	89
8	KCl	0.5	50	72
9	NaCl	0.5	50	70
10	NaBr	0.5	50	65
11	NH ₄ Cl	0.5	50	6
12	Na ₂ CO ₃	0.1	50	99
13	Na ₂ CO ₃	0.2	50	94
14	Na ₂ CO ₃	1	50	95
15	Na ₂ CO ₃	0.1	25	86
16	Na ₂ CO ₃	0.1	60	99
17 ^[c]	Na ₂ CO ₃	0.1	50	90
18	Na ₂ CO ₃	0.1	70	96
19 ^[d]	Na ₂ CO ₃	0.1	50	< 5

[a] Reaction conditions: Fe^{III}Mo₆ (0.1 mol %), benzaldehyde (1.5 mmol), O₂ (1 atm), additive (0.1 equiv), H₂O (2 mL), unless otherwise noted.

[b] Yields were calculated from ¹H NMR spectra. [c] Reactions were carried out under atmospheric air. [d] Reactions were carried out under nitrogen atmosphere.

atmospheric pressure also gave the oxidized product in 90 % yield (entry 17). When the reaction was carried out under nitrogen atmosphere, a very low yield was obtained (< 5 %), thus reflecting a stoichiometric aldehyde oxidation (entry 19). As a control experiment, only a trace amount of the product was detected when the reaction was carried out in the absence of the Fe^{III}Mo₆ catalyst.

With the optimized reaction conditions in hand, the scope and functional-group compatibility of this methodology were then examined using a number of functionalized aldehydes (Table 2). To our satisfaction, excellent yields were obtained with all aldehydes that we examined. Aromatic aldehydes bearing a hydrocarbon R group (benzaldehyde, *p*-tolualdehyde, 4-isopropylbenzaldehyde, 1-naphthaldehyde, or 2,4,6-trimethylbenzaldehyde) were all oxidized in quantitative yields (products **1–6**). Halogen-substituted aldehydes such as 4-fluorobenzaldehyde, 4-chlorobenzaldehyde, 4-(trifluoromethyl)benzaldehyde, and 5-bromo-2-chlorobenzaldehyde were tolerated under the optimized reaction conditions, and the corresponding carboxylic acids were obtained in quantitative yields regardless of the location of the substituent (**7–10**). Electron-poor aromatic aldehydes, for example 4-nitro-substituted benzaldehydes, were highly amenable to the reaction conditions and were oxidized to the corresponding products with near quantitative yield (**12**). The electron-rich aromatic aldehydes, mono- and di-methoxy-substituted benzaldehydes, were also oxidized in quantitative yields (**13** and **14**). It is worth noting that 4-formylbenzoic acid, 4-hydroxybenzaldehyde, and 2-hydroxybenzaldehyde undergo near

Table 2: Investigation of substrate scope.^[a]

[a] Reaction conditions: Fe^{III}Mo₆ (0.1 mol%), aldehydes (1.5 mmol), O₂ (1 atm), Na₂CO₃ (0.1 equiv), and H₂O (2 mL). Yields are those of the isolated products.

quantitative conversion into their respective carboxylic acids, without the need for carboxy and hydroxy protection (**11**, **15**, and **16**). All aryl-substituted conjugated cinnamaldehydes bearing electron-donating and electron-withdrawing groups were oxidized quantitatively, irrespective of the position of the substituent on the aryl ring (**17–22**). Various aliphatic aldehydes were also tested: propionaldehyde, butyraldehyde, pentanal, and octanal were oxidized with 96, 96, 98, and 99% yields, respectively (**23–26**). An aldehyde containing a carboxy or carbonyl moiety, 3-oxopropanoic acid and 4-oxopentanal, respectively, gave the corresponding products in quantitative yield (**27** and **28**). Similarly, branched pivalaldehyde, 2-methylpentanal, 2-chloropropanal, and cyclohexanecarbaldehyde also gave quantitative yields (**29–32**). With a C=C

bond being nonconjugated or conjugated to the carbonyl, acrylaldehyde, (2*E*,4*E*)-hexa-2,4-dienal, and cyclohex-3-enecarbaldehyde, the oxidation proceeded quantitatively (**33–35**). Heterocyclic aromatic aldehydes such as 2-furaldehyde, nicotinaldehyde, and 2-thiophenecarboxyaldehyde were also oxidized with essentially quantitative yields of products (**36–38**). Finally, a gram-scale reaction was conducted with 0.1 mol% of catalyst and 2.65 grams (25.0 mmol) benzaldehyde in 5 mL water. Analytically pure benzoic acid was isolated in 91% yield after 20 hours (Figure 3). The ability of the Fe^{III}Mo₆ POM catalyst to be recycled and used in successive reactions was also evaluated. The solid catalyst was isolated by filtration and used directly for subsequent oxidations of benzaldehyde without further purification (following the addition of ether to the hydrophobic organic products). The Fe^{III}Mo₆ catalyst could be reused at least eight times without any degradation in catalyst performance (Table 3). To confirm the high stability of the catalyst and its associated performance, the structure and morphology of the catalyst were further investigated using FTIR and ¹H NMR spectroscopy. The structure and morphology of the recycled catalyst remains unchanged from its initial state (see Figures S1 and S2 in the Supporting Information).

On the basis of the results of our study and the iron enzyme catalysts reported,^[20] a tentative mechanism that rationalizes the

product formation is illustrated in Figure 4. Note that any comment on the specific details of the mechanism is speculative at this stage. First, the active iron catalyst intermediate **A** is generated through activating the dioxygen molecule with the help of catalyst's hydrogen proton, and the

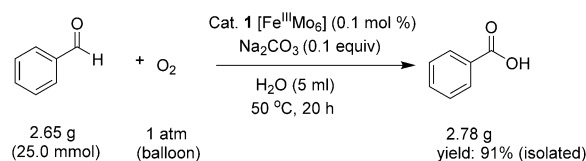
**Figure 3.** Gram-scale reaction.

Table 3: Recycling experiments of catalyst.^[a]

Run time	1	2	3	4	5	6	7	8
Yield [%] ^[b]	99	99	99	99	99	97	97	96

[a] Reaction conditions: Fe^{III}Mo₆ (0.1 mol%), benzaldehyde (1.5 mmol), O₂ (1 atm), Na₂CO₃ (0.1 equiv), H₂O (2 mL). [b] Unless otherwise noted, yields are those of the isolated products.

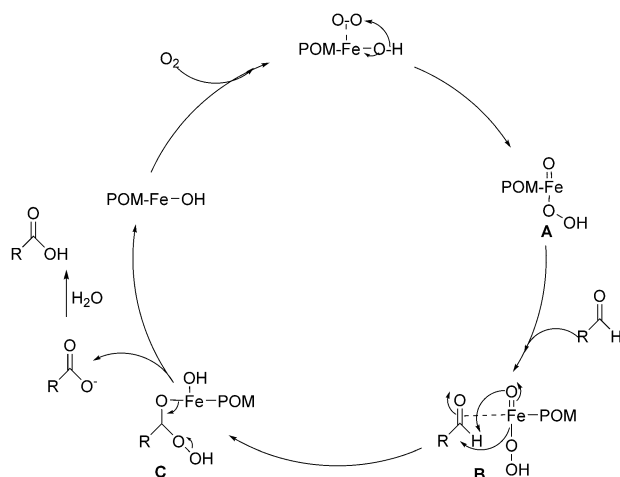


Figure 4. Proposed mechanism for the Fe-POM-catalyzed oxidation of aldehydes in water.

high-valent species favor oxidation of aldehydes, its role is similar to the iron enzyme catalyst in the catalytic oxidation reaction.^[21] The intermediate **A** subsequently coordinates to the C=O bond of the aldehyde and affords the intermediate **B** and exchanges its coordinated OH with the H of the aldehyde simultaneously to give the intermediate **C**, possibly through a nucleophilic attack of OH followed β -hydride elimination. Finally, **C** releases the carboxylic acid as the product and closes the catalytic cycle.

In summary, we have developed the first example of a catalytic aerobic oxidation of aldehydes in water using an organic-hybrid iron-Anderson POM catalyst. The reaction can be conducted using 1 atm oxygen gas as the oxidant. A number of aldehydes have been successfully transformed into the corresponding carboxylic acids with excellent yields. This reaction occurs at a very mild temperature and can be carried out with an extremely low loading of the Fe^{III}Mo₆ POM catalyst, even on a gram scale. These excellent results, together with its operational simplicity and the ability to successively reuse the catalyst, make this new methodology environmentally benign and cost effective. The generality of this methodology gives it the potential for use on an industrial scale. Further investigations concerning the mechanism of the reaction and other potential applications of the Fe^{III}Mo₆ POM catalyst are currently under way in our laboratory.

Experimental Section

General Procedure for the oxidation of aldehydes: Fe^{III}Mo₆ (2.72 mg, 0.0015 mmol, 0.1 mol%), benzaldehyde (159.0 mg, 1.5 mmol), O₂ using a balloon (1 atm), Na₂CO₃ (15.9 mg, 0.15 mmol,

0.1 equiv), and H₂O (2 mL) were added in a tube. The mixture was stirred at 50 °C, and the reaction progress was monitored by TLC and GC-MS. After completion of the reaction, 3 × 2 mL of ether and CH₃CN were added, the solid catalyst was isolated by filtration and used in subsequent reactions. The reaction mixture was extracted with ethyl acetate (3 × 5 mL), dried over anhydrous Na₂SO₄, and evaporated in vacuo to obtain the carboxylic acid product.

Acknowledgments

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Conflict of interest

The authors declare no conflict of interest.

Keywords: iron · molecular oxygen · oxidation · polyoxometalates · water

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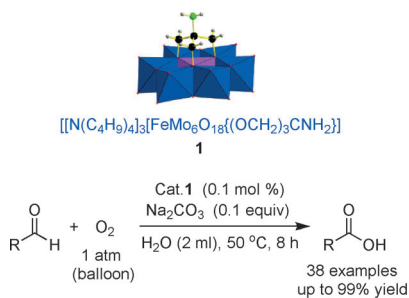
Communications



Heterogeneous Catalysts

H. Yu, S. Ru, G. Dai, Y. Zhai, H. Lin,
S. Han,* Y. Wei* ———— ■■■■—■■■

An Efficient Iron(III)-Catalyzed Aerobic
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Ironclad: A heterogeneous aerobic oxidation of aldehydes in water was developed with a polyoxometalate-based iron catalyst. This method utilizes 1 atmosphere of oxygen as the sole oxidant, proceeds under extremely mild aqueous conditions, and covers a wide range of various functionalized aldehydes.