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ARTICLE



Highly Efficient Oxidation of Alcohols to Carboxylic Acids Using Polyoxometalate-supported Chromium(III) Catalyst and CO₂

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Direct catalytic oxidation of alcohols to carboxylic acidsis very attractive, but the economical-friendly catalysis systems have not yet well established. Here, we show that a pure inorganic ligand-supported chromiumcompound, $(NH_4)_3$ [CrMo₆O₁₈(OH)₆] (simplified as CrMo₆), could be used to effectively promote this type of reaction in the presence of CO₂.In almost all cases, the oxidation of various alcohols (aromatic and aliphatic) could be achieved under mild conditions, and corresponding carboxylic acids can be achieved in high yield. The chromium catalyst **1** can be reused for several times with little loss of the activity. Mechanism study and control reactions demonstrate that the acidification proceeds*via* the key oxidative immediate of aldehydes.

Introduction

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Selective oxidation of alcohols to carboxylic acids is an important process for the synthesis of various fine chemicals in the chemical industry, and has been kept a difficult task in the field of green organic synthesis.¹Traditionally, stoichiometric, toxic and expensive oxidants, such as $KMnO_4^2$ and CrO_3^3 , have often been used to complete this conversion, resulting in significant waste. Therefore, it is highly desirable to develop an environmentally friendly new oxidation scheme. Compared with traditional oxidants, the cheap, abundant and non-toxic nature of CO₂ has brought great interest to its use as an accelerator in oxidation reactions, including the oxidative dehydrogenation of alkanes, the oxidation of CH₄, alkyl aromatics, C-C bond formation between aldehydes and the like.⁴Although metal-ligand complexes have become a mature technology for the selective catalytic oxidation of alcohols to aldehydes,⁵ there are few reports on the oxidation of alcohols directly to carboxylic acids. In that case, the preparation of carboxylic acids still remains a fundamental challenge. Even with the use of precious metal catalysts, the success or scope of preparation is quite limited.⁶⁻¹⁴In addition, a common feature of these catalytic systems is that they use complex and unavailable organic ligands to increase catalytic activity and selectivity. Due to the sensitivity of organic ligands to oxidative self-degradation, the durability and recyclability of organometallic catalysts under mild conditions remain a major challenge in industrial and synthetic

chemistry.¹⁵

Polyoxometalates (POMs)^{16,17}, as a class of metal-oxide clusters with unmatched structural diversity and functionality, are considered to be an inorganic alternative to classical transitionmetal complexes. The catalytic function of POMs has attracted much attention because their ability to design catalytically active sites allows for 'fine-tuning' of their redox and acidic properties at the atomic or molecular levels¹⁸. Recently, our group reported that Anderson-typePOMs¹⁹ can be used as the inorganic ligandsupported metal catalysts²⁰ for the highly efficient aerobic oxidation of aldehydes to carboxylic acids, amines to imines or formamides, and alcohols to aldehydes/ ketones. These types of inorganic ligandsupported metal catalysts possess a unique structure with a single central metal atom supported by an inorganic ring made up of six edge-sharing Mo^{VI}O₆ octahedral scaffolds; this greatly enhances the Lewis acidity of catalytically active sites, as well as enables the edge-sharing MoO₆ unit to act as ligand analogues to those used in traditional organometallic complexes. Inspired by this, the versatile tunability of Anderson-type POMs prompts us to further extend the scope of this type of catalysts for other catalytic oxidative transformations.



Scheme 1Oxidation of alcohols into carboxylic acid

Herein, we report that an inorganic-ligand supported chromium catalyst **1**, $(NH_4)_3[CrMo_6O_{18}(OH)_6]^{21}$ (Scheme1), which possess the chromium(III) ion core and can be readily synthesized in one pot in aqueous solution (see supporting information, Figure S1), can efficiently catalyse the oxidation of various alcohols into carboxylic acids in the presence of CO_2 withhigh catalytic activity and good selectivity. More importantly, **1** could be recycled and reused for at least six times with negligible loss of activity due to high stability. One of the main advantages of this catalytic system is

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that it can avoid the use of complicated/sensitive organic ligands. Mechanistic insight based on the observation of key intermediate and control reactions will be also presented.

2 Results and discussion

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Initially, our studies began with the oxidation of salicyl alcoholas a model substrate using one atmospheric pressureCO2at 80 °Cin a solution of DMSO for 24h to assess the catalyst 1. And the efficiency of the transformation is clearly strongly affected by the presence of inorganic salt(Table 1, entries 1 and 2). The reaction with the presence catalyst1 resulted in the formation of salicyl acid in 85% yield after 24h. In contrast, we found that replacing the centric chromium atom with other metals such as iron and nickel, a very low and not that high yield (< 10%) was obtained under the same conditions, being indicative of the key role of chromium in catalysis. When the reaction was carried out with N₂orO₂instead of CO₂, a very low and not that high yield was obtained (entries5 and 6), reflecting a stoichiometric alcohol oxidation. Since we have conducted several reactions with different additives, such as KCl, NaCl, ZnCl₂ and so on, the results showed that only K₃PO₄ gave the optimized yield under the same reaction conditions (see in SI, Table S1).We propose that CO₂ promoted the oxidation of alcohol to acid in the presence of a base. And considering that the phosphate provides a relatively large number of oxidizing products which is most likely attributed to the PO43-acted as an electron-transfer mediator to improve the electron transfer efficiency. Thus, Potassium phosphate was selected as the salt for optimizing the conditions.

		Standed Conditions		
~ОН	CO (1.0 bor)	Cat. 1 (1.0 mol %) K ₃ PO ₄ (0.1 equiv.)	ОН	
∕_ОН +	(balloon)	DMSO (2.0 ml), 24 h, 80 °C	СН	
Entry	Variation	Yield		
	conditions		(%) ^a	
1	None		85(79)	
2	W	-		
3	N ₂ (1.0 bar) ii	<5		
4	O ₂ (1.0 bar) i	53		
5	Cr(NO ₃) ₃ .6	Trace		
6	(NH ₄) ₆ Mo ₇ O ₂	Trace		
7	Cr(NO ₃) ₃ .6H ₂	<10		
8	Without K ₃ PO ₄ 37			
^a Yields were determined by GC-MS analysis of the crude				

reaction mixtures, values in parentheses are the isolated yields.

We then tested different loading amount of catalyst, temperature, also including the effect of solvent and time(Table S1),and found that the best results being obtained in 85% yield and 99% conversion of the desired product with 1.0 mol% of chromium catalyst in DMSO at 80 °C for 24 h. As a control experiment, only atrace amount of the product was detected in the absence of the chromium catalyst(entry 2). It should be noted that when Cr(NO)₃, or (NH₄)₆Mo₇O₂₄ also considered to be an isomerized Anderson-structured POM with an Mo core instead of Cr as the central atom was used as the catalyst alone, no product was provided(for

example, entries 5 and 6). The superior oxidation efficiency of the combined catalyst platform indicates that every constituent plays a vital role in the inorganic-ligand supported chromium catalysis.

Table 2 CO2 and POM-Cr^{III}-catalyzed oxidation of various alcohols ^{ab}



^aUnless otherwise stated, all reactions were carried out under following conditions: Cat. **1** (1.0 mol %), alcohols (1.0 mmol), CO_2 (1.0 bar), K_3PO_4 (0.1 equiv.), and DMSO (2.0mL) at 80°Cfor 24 h. ^bYields were determined by GC-MS and¹H NMR, values in parentheses are the isolated yields.

With the optimized reaction conditions in hand, the scope of alcohols was investigated (Table2). To our delight, various substituted aromatic and aliphatic alcohols could be smoothly converted to the corresponding acids in remarkably high yields. Aromatic alcohols bearing a hydrocarbon R group (benzyl alcohol, *p*-toluic alcohol, 4-isopropylbenzyl alcohol, 2,4,6-trimethylbenzyl alcohol, naphthalene methanol) were all oxidized in quantitative yields (2-4, 11and 13). Halogen-substituted alcohols such as 4bromobenzyl alcohol, 4-chlorobenzyl alcohol, 4-fluorobenzyl alcohol, 4-(trifluoromethyl) benzyl alcohol and 4-bromo-2-chlorobenzyl alcohol were tolerated under the optimized reaction conditions, and the corresponding carboxylic acids were obtained in quantitative yields regardless of the location of the substituent (6-9 and 14). Electron-poor aromatic alcohols, for example 4nitrosubstituted benzyl alcohol, were highly amenable to the reaction conditions and were oxidized to the corresponding products with near quantitative yield (10). The electron-rich aromatic alcohols, mono- and di-methoxy-substituted benzyl alcohols, were also oxidized in quantitative yields (5 and 12). It is worth noting that 4-hydroxy-3-methoxybenzyl alcohol and 2hydroxybenzyl alcohol undergo near quantitative conversion into their respective carboxylic acids, without the need for carboxyl and hydroxyl protection (15-16). All aryl-substituted conjugated cinnamyl alcohols bearing electron-donating and electronwithdrawing groups were oxidized quantitatively, irrespective of the position of the substituent on the aryl ring (17-23). Various aliphatic alcohols were also tested and gave the corresponding

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products in quantitative yield (28-32). Similarly,2-chloro-2propanolandcyclohexanemethanol also gave quantitative yields (34-35). Heterocyclic aromatic alcohols such as 3-(hydroxymethyl) pyridine, furfuryl alcohol, 2-thiophenemethanol and 4-methyl-5thiazoleethanolwere also oxidized with essentially quantitative yields of products (24-27). Finally, a gram-scale reaction was conducted with 1.0 mol% of catalyst and1.34 grams (10.0 mmol) alcohol in 20.0mL DMSO. Analytically pure benzoic acid was isolated in 88% yield after 24 hours (Figure S4).

The catalyst-recycling experiments were also performed. The solid catalyst was isolated by filtration and was used directly for subsequent oxidation of alcohols without further purification (other than the addition of ether to remove the hydrophobic organic products). The catalyst could be used at least five times without any degradation in catalyst performance during the reaction. Since POM has several unique properties because of its structure, certain polar molecules (such as alcohols and amines) can freely enter and exit the body phase of POM at room temperature, making it have a liquid phase-like reaction characteristic, which is called "pseudoliquid-phase behavior".²²The catalyst we used is soluble in DMSO at 80°C. As a result, after the reaction completed, we need to get it filtrated from the system by simply adding ethyl acetate to the reaction system after the oxidative experiments and the solid catalyst was reused for next run. For the 6th run of the recycling experiment, the yield of the acid was 78% which implied the robustness and good stability of the catalyst (Figure S5). 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 XRD spectroscopy. The structure and morphology of the recycled catalyst remains unchanged from its initial state (Figures S6 and S7).

Control experiments					
			Cat. 1(1.0 mol %)		
			CO ₂ (1.0 bar, balloon)		
		TEMPO(0.1equiv)	K ₃ PO ₄ (0.1 equiv)		
(a)	PhCH ₂ OH +	or	DMSO, 24 h, 80 °C		
	1.0 mmol	BHT(0.1equiv)	trace		
			Cat. 1(1.0 mol %)		
			CO ₂ (1.0 bar, balloon)		
(1-)			K ₃ PO ₄ (0.1 equiv)		
(D)	FIGH2011 -01	OF PIICH2OD	DMSO 24 h 80 °C		
	1.0 mmol	1.0 mmol	KIE-K /K = 1.06		
			$RIE = R_{H} R_{D} = 1.00$		
			Cat. 1(1.0 mol %)		
			CO ₂ (1.0 bar, balloon)		
(c)	PhCH ₂ OH	+ PhCH ₂ OD	K ₃ PO ₄ (0.1equiv)		
(0)					
	0.5 mmol	0.5 mmol	LINISO, 24 11, 60 °C		
			NIE - NH ND = 0.00		

Figure 2 Control experiments

To investigate the mechanism, several control experiments were conducted (Figure 2). When 0.1 mmol Cr-catalyst 1 is used under an CO2 atmosphere at 80°C for 6 hours, according to Das group's outstanding resaerch,4eweproposed that key features were the formation of an intermediate carbonate ester followed by nucleophilic substitution by DMSO and finally deprotonation and proton shift which led to the benzaldehyde formation. And then the chromium catalyst 1 activates the further combination of the product. The presence of trapping agents (such as BHT or TEMPO) strongly suppressed the carbonyl compound formation, which indicated that a free radical pathway may be involved in the present oxidation reaction (Figure 2a). The kinetic isotope effect (KIE) was investigated with respect to both alcoholic O–H/D bonds and benzylic C(sp3)-H/D bonds. A clear kH/kD value of 1.02 was determined bytwo independent reactions using benzyl alcohol-H and benzyl alcohol-D as the substrates (Figure 2b). The intermolecular kH/kD value for benzyl alcohol-H and benzyl alcoholD was determined to be 5.26 (Figure 2c). Taken together these experimental results suggested that the deavage of the deavage

The ¹H NMR studies that the progress of the oxidation of benzyl alcohol in the presence of K_3PO_4 as an additive was also carried out as shown in Figure 3. To our delight, the production of benzoic acid (12.89 ppm) was detected after 16h, and benzaldehyde as the only intermediate product, was also observed (10.03 ppm). The characteristic peaks of benzyl alcohol and benzaldehyde in the reaction system gradually decreased, and benzyl alcohol almost disappeared completely when the reaction time was prolonged to 24h. And also a significant proportion of benzoic acid can be detected in the system then.

On the basis of the above experiments, polyoxometalate catalysts reported,^{23,24}we proposed the mechanism in Figure4.Firstly, the formation of carbonate ester is required to transform the hydroxyl group into a better leaving group. And we find that the key features are the formation of an intermediate carbonate ester followed by nucleophilic substitution by DMSO and finally deprotonation and proton shift which leads to the aldehyde intermediate.^{4e}And then the chromium catalyst **1** activates the intermediate to be further oxidized to carboxylic acid.







Figure 4 Proposed mechanism for POM-Cr(III)-catalyzedoxidation of alcohols.

4 Conclusions

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In summary, we described here that the pure inorganic ligand supported chromium catalyst **1** can promote the direct oxidative acidification of a variety of alcohols in the presence of CO_2 as green promoter. Both oxidation of aromatic and aliphatic alcohols proceed quite smoothly under mild conditions, affording the corresponding carboxylic acid products very efficiently. The chromium catalyst is stable and recyclable, and can be easily prepared by a simple one-step synthesis from simple inorganic metal salts. Furthermore, the catalysis is achieved high efficiently in the absence of any organic ligands. We envision that this simple, effective and environmentally benign methodology can be potentially used for various synthetic procedures.

Conflicts of interest

There are no conflicts of interest to declare.

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A green and highly efficient oxidation of alcohols to carboxylic acids using polyoxometalate-supported chromium(III) catalyst and CO₂