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Polyoxometalate compound: a highly efficient heterogeneous catalyst for aerobic alcohol oxidation

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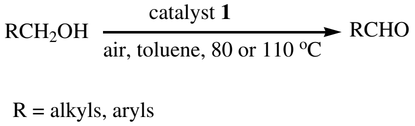
Abstract—Oxidation of alcohols to aldehydes and ketones has been studied using atmospheric oxygen and a catalytic amount of $Na_{6.3}Fe_{0.9}[AlMo_{11}O_{39}]\cdot 2H_2O$ in toluene under heating (80 or 110 °C) in high yields. Secondary alcohols can be chemoselectively converted into ketones in the presence of primary hydroxyl groups.

The oxidation of alcohols into the corresponding aldehydes or ketones is one of the most important functional group transformations in organic synthesis.[1] Recently, the use of molecular oxygen as terminal oxidant has received great attention for both economic and environmental benefits, and many highly efficient systems have been developed for catalytic aerobic alcohol oxidation using Pd,[2] Ru,[3,14,20] Cu,[4] Co,[5] V,[6] Ph,[7] Os,[8] Ni,[9] Zr,[10] M(II)-radical catalysts,[11] M-TEMPO,[12] polyoxometalates,[13] Ru-biomimetic-coupled systems,[14] bimetallic Mo–Cu,[15] and Os–Cu[16] systems, perruthenate,[17] Pt, and Pt/Bi catalysts,[18] manganese oxide octahedral molecular sieves,[19] Ru-hydroxyapatite,[20] lignin peroxidase,[21] Noble-metal,[22] polymer encapsulation of metallophthalocyanines,[23] and others.[24]

Although these procedures for the oxidation with air/molecular O_2 are efficient, most of them are homogeneous systems and share common drawbacks because of which catalyst/product separation and catalyst reuse are difficult. The immobilization (heterogenization) of catalytically active species onto solid supports (insoluble bulk materials, inert solid supports such as metal hydroxides and polymers) display advantages, for example, no co-catalyst requirement and convenient separations, but their applications are limited, either to activated alcohols or by the need for pure oxygen. However, a major challenge in liquid-phase oxidation with these systems is to prevent leaching of the active species. The search for suitable green aerobic catalysts is still a significant challenge.

In this letter, we report a highly efficient catalytic system made up of a novel polyoxometalate catalyst **1** ($Na_{6.3}Fe_{0.9}[AlMo_{11}O_{39}]\cdot 2H_2O$): A solid catalyst is indiscerptible in both water and organic solvents which has high selectivity and are active for the aerobic oxidation of a variety of alcohols (Scheme 1). Catalytic results indicate that the polyoxometalate catalyst is a green, selective, and efficient aerobic catalyst for alcohol oxidation. It can selectively oxidize alcohols to their corresponding carbonyls under mild aerobic conditions without using sacrificial reducing agents and pure O_2. This reaction system displays an important merit, that is, more facile catalyst/product separation and catalyst reuse.

Preparation of catalyst precursor ($Na_{3.5}H_{5.5}AlMo_{11}O_{39}\cdot 9H_2O$): Sodium molybdate (13.3 g, 55 mmol) is dissolved in 30 ml of water in a separate 100 ml beaker containing a magnetic stirring bar. To this solution,



$$RCH_2OH \xrightarrow[\text{air, toluene, 80 or 110 °C}]{\text{catalyst } \mathbf{1}} RCHO$$

R = alkyls, aryls

Scheme 1.

Keywords: Indiscerptible polyoxometalate; Oxidation of alcohol; Atmospheric oxygen; Catalyst separation.

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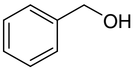
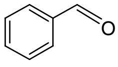
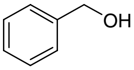
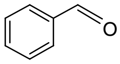
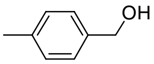
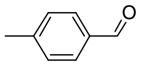
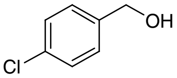
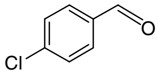
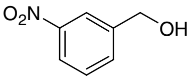
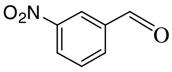
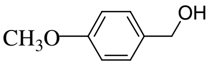
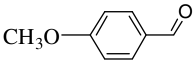
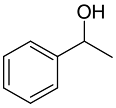
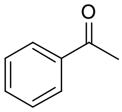
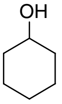
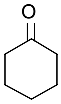
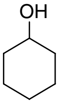
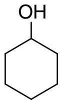
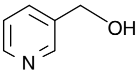
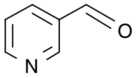
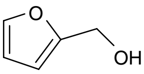
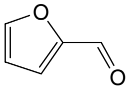
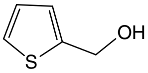
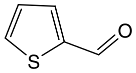
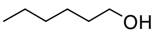
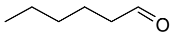
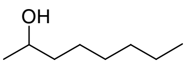
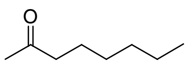
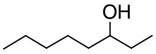
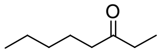
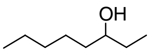
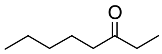
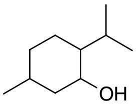
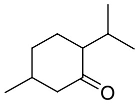
Table 1. Selective oxidation of alcohol with air by $Na_{6.3}Fe_{0.9}[AlMo_{11}O_{39}]·2H_2O$[a]

Entry	Substrate	Method	Time	Product	Yield (%)	Selectivity (%)	TON
1[b]		A	1		69	99	138
2		A	1		96	99	192
3		A	1		96	99	192
4		A	1		93	99	186
5		A	4		87	99	43.5
6		A	1		98	99	196
7		A	3		98	99	65.3
8		A	9		93	99	21.7
9		B	3		94	99	65
10		B	4		90	99	45
11		A	1		97	99	194
12		A	4		95	99	190
13		B	6		88	99	29
14		B	5		92	99	20
15		B	5		89	99	36
16		B	5		88	99	35
17		B	4		92	99	46

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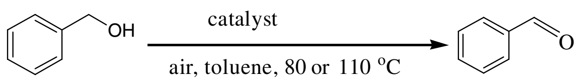
[a] Reaction conditions: alcohol (2 mmol), catalyst (0.01 mmol), toluene (6 ml), atmospheric pressure; method A: 80 °C (oil bath temperature); method B: 110 °C (oil bath temperature). Selectivities are based on the GC with area normalization. All yields are for pure, isolated products.

[b] $Na_{3.5}H_{5.5}AlMo_{11}O_{39}·9H_2O$ as catalyst.

Table 2. Recycling of the catalytic system for the oxidation of benzyl alcohol to aldehyde[a]



Run	Time	Conversion (%)	Yield (%)
1	1	100	96
2	1	100	95
3	1	100	96

[a] Reaction conditions: alcohol (2 mmol), catalyst (0.01 mmol), toluene (6 ml), atmospheric pressure, 80 °C (oil bath temperature). Selectivities are based on the GC with area normalization. All yields are for pure, isolated products.

16.5 ml of 4 M HCl is added in 1 ml portions over 1 min, with vigorous stirring. Then, a solution containing $Al(NO_3)_3{\cdot}9H_2O$ (1.89 g, 5 mmol) is poured into the molybdate solution, and pH is adjusted to between 2 and 3 by addition of the 4 M HCl. The solution is kept at 90 °C for 1 h. The yellow crystal is collected at room temperature. IR (KBr, ν/cm^{-1}) 1053.71, 956.27, 880.51, 784.13, 701.08, 627.12, 577.28.

Preparation of catalyst ($Na_{6.3}Fe_{0.9}[AlMo_{11}O_{39}]{\cdot}2H_2O$): 3 g of yellow crystal ($Na_{3.5}H_{5.5}AlMo_{11}O_{39}{\cdot}9H_2O$) is dissolved in 20 ml water in a separate 100 ml beaker containing a magnetic stirring bar. To this solution, a solution of 0.55 g $Fe(NO_3)_3{\cdot}6H_2O$ is added. The solution is kept at room temperature for 1 h. The yellow solid product is collected on a sintered glass funnel, washed with water and acetone, dried in air. IR (KBr, ν/cm^{-1}) 1036.10, 970.77, 912.04, 708.93, 661.44, 506.55.

To begin with, the oxidation of benzyl alcohol was examined as a standard substrate in the presence of a catalytic amount of **1** in toluene under air pressure. As expected, the oxidation took place affording benzaldehyde in 99% yield when the reaction mixture was allowed to stir at 80 °C for 1.0 h. In contrast, the corresponding homogeneous process using $AlMo_{11}O_{39}$ was less effective and provided benzaldehyde only in 69%. This suggested that Mo ions in the polyoxometalate catalyst play a key role for the aerobic alcohol oxidation, and Fe ions could adjust Lewis acidity and redox of the catalyst and improve catalytic activity.

To study the scope of this procedure, the oxidation of other alcohols was next studied (Table 1, entries 1–15). All benzylic alcohols having electron-withdrawing and -donating groups in the aromatic ring, that is, 4-chloro-, 3-nitro-benzyl alcohols were converted into their corresponding aldehydes in high isolated yields within 2 h. Compared to benzylic alcohols, aliphatic alcohols showed relatively low activities in the oxidation. To address this, we rose the temperature to 110 °C to improve the reaction rate. Under these modified conditions, the oxidation of 1-hexanol can be completed within 3 h. Secondary alcohols such as phenylethanol, 2-octanol, and cyclohexanol required a slightly longer reaction time compared to benzylic alcohols to afford the corresponding ketones in 88–92% yields. Heterocyclic alcohols, 2-thiophenemethanol, and 2-pyridinemethanol, were oxidized to the corresponding aldehydes in high yields. No oxidation was observed with S and N heteroatoms. In addition, a mixture of primary and secondary alcohols was next subjected to oxidation. When cyclohexanol and hexyl alcohol were allowed to react, the former oxidized to cyclohexanone in 90% yield and the latter gave hexanal in <10% yield. This clearly reveals that this method can be applied for the chemoselective oxidation of secondary alcohols in the presence of primary hydroxy groups.

Furthermore, a catalyst recycle experiment (2 mmol of benzyl alcohol, 6 ml of toluene, 80 °C, 1 h) carried out simply by filtration of catalyst and re-addition of benzyl alcohol (2 mmol) showed 96%, 95%, and 96% yields in three reaction cycles with benzaldehyde as the only product. There was no discernible loss in activity or selectivity. To confirm whether the oxidation proceeded heterogeneously, we have checked the progress of the oxidation of the filtrate under the similar reaction conditions; Al, Mo, and Fe ions in the solution could not be detected by ICP analysis after the alcohol oxidation reaction.

In conclusion, the oxidation of alcohols to aldehydes and ketones has been studied with molecular oxygen in the presence of recyclable catalyst **1** in high yields. This reaction provides a new environmentally friendly route to the conversion of alcoholic functions to carbonyl groups. Aldehydes do not undergo further oxidation to carboxylic acids.

Typical procedure for the oxidation: Alcohol (2 mmol) and catalyst **1** (0.01 mmol) were stirred at 80 °C in toluene (6 ml) under air pressure for the appropriate time (Tables 1 and 2). After filtering the catalyst, the filtrate was analyzed by GC and passed through a short pad of silica gel using ethyl acetate and hexane (1:19) as eluent or distilled to provide the analytically pure aldehydes and ketones.

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