

## A FACILE, SELECTIVE AEROBIC OXIDATION OF ALCOHOLS OVER COMMERCIAL ACTIVATED CARBON

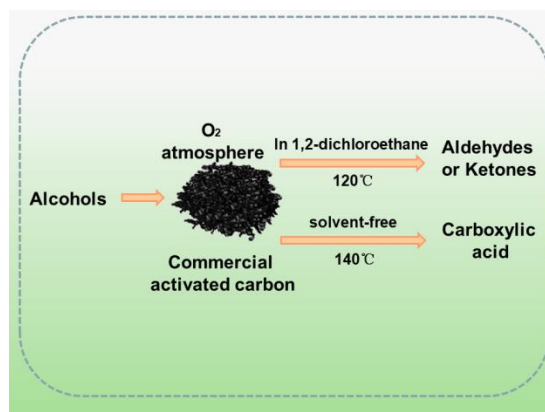
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Commercial activated carbon without any modification was successfully applied to aerobic oxidation of alcohols. The activity test confirmed that commercial activated carbons possessed tangible catalytic activities. Aldehydes/ketones and carboxylic acids were selectively furnished on activated carbon in the presence/absence of solvent. Compared to the metal catalyst, activated carbon had advantages of excellent availability, low cost, environmental benignity and good reproducibility. Our procedure provided an alternative for the selective aerobic oxidation of alcohol.



### INTRODUCTION

Selective catalytic oxidation of alcohols to corresponding carbonyl compounds is of great importance for both academia and industrial production.<sup>1,2</sup> Classical oxidation methods feature a strong oxidizer, such as ClO<sup>-</sup>, Cr<sup>IV</sup>, Cl<sub>2</sub>, or peroxy acids, which are corrosive and toxic.<sup>3</sup> Therefore, exploration for an alternative method utilizing green oxidants is necessary.

Molecular oxygen (O<sub>2</sub>) is an ideal and quintessential oxidant, which is clean, atomically economical and the cheapest oxidizing agent. Unfortunately, the activation of O<sub>2</sub> is difficult; it requires the catalysts with high catalytic

performance. Extensive efforts have been undertaken to explore efficient catalysts. And, considerable advancement has indeed been made; various catalytic systems including noble metal (Au,<sup>4</sup> Pt,<sup>5</sup> Pd,<sup>6</sup> Ru<sup>7</sup>) and non-noble metal (Cu,<sup>8</sup> Mn,<sup>9</sup> Ni,<sup>10</sup> Co,<sup>11</sup> Fe<sup>12</sup> etc.) have been developed. These metal catalytic systems exhibit considerable success, whereas there are still different levels of shortcomings or limitations, such as high cost, laborious catalyst fabrication, metal pollution.

Recently, metal-free carbon-based materials have attracted great interest in catalysis due to low price, rich defect sites, tunable electronic structure, environmental acceptability, corrosion resistance,

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thermal stability, etc.,<sup>13-15</sup> showing a potential to develop new generation of catalysts. Doped graphenes and carbon nanotubes (CNTs) have been developed to catalyse oxidation of alcohols.<sup>16-20</sup> Undoubtedly, the use of metal-free catalysts is a great progress for alcohol oxidation.

Activated carbon (AC), as a mass produced carbon-based material, is widely used in different application fields because of unique physicochemical properties, low cost and non-pollution.<sup>21-25</sup> Herein, commercial AC was employed as metal-free catalyst for the selective aerobic oxidation of alcohols into aldehydes and carboxylic acids, thereby avoiding laborious fabrication procedures of graphenes or CNTs.

Reaction condition are investigated in details; the oxidation process of alcohols was controlled to selectively furnish aldehydes and carboxylic acids in solvent/ solvent-free condition. Our procedure possessed the merits of cost effectiveness, easy work up and environmental benignity.

## EXPERIMENTAL

### Materials

Activated carbons were purchased on the market. For convenience, different activated carbons were numbered Cx. The details of the activated carbon samples were as follows:

Activated carbons	Morphology	Sources	Producers
C <sub>1</sub>	Powder	Unknown	Xilong Scientific Co., Ltd
C <sub>2</sub>	Powder	Petroleum coke	Fuchen Chemical Reagent Co., Ltd
C <sub>3</sub>	Powder	Bamboo	Laiyang Economic and Technological Development Zone Fine Chemical plant
C <sub>4</sub>	Powder	Nut shell	Xichun Environmental Protection Technology Co., Ltd
C <sub>5</sub>	Powder	Coal	Shenzhen Xingwanbang Activated Carbon Co., Ltd
C <sub>6</sub>	Columnar	Coal	Fujian Xinyao Trading Co., Ltd
C <sub>7</sub>	Bulk	Charcoal	Tianda Carbon Industry Co., Ltd
C <sub>8</sub>	Granular	Unknown	Tianjin Beichen Founder Reagent Factory
C <sub>9</sub>	Granular	Petroleum coke	Jingke Chemical Co., Ltd
C <sub>10</sub>	Columnar	Bamboo	Qingdao Jielong Chemical Co., Ltd
C <sub>11</sub>	Spherical	Charcoal	Jiangxi Longsheng Activated Carbon Co., Ltd

Other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and Shanghai Macklin Biochemical Co., Ltd.. Beyond that, all the reagents were used without further purification.

### Typical procedure for aerobic oxidation of alcohols to aldehydes/ketones

The oxidation reaction was carried out in a 25 mL round bottomed flask equipped with a condenser. Benzyl alcohol (5 mmol), 1, 2-dichloroethane (1g) and AC (0.5g) were added and the mixture was stirred at 120 °C under O<sub>2</sub> atmosphere for a given period of time. After the completion of the reaction, the temperature was cooled to 80 °C, and 1, 2-dichloroethane (10 mL) was added into the mixture for an hour until the product was completely dissolved. Then filtration was conducted to separate the solid catalyst, and the obtained residue was washed by 1, 2-dichloroethane to completely extract the organic compound. The 1, 2-dichloroethane extract mixtures were collected together and analysed by using Agilent GC-MS 7890 and Shimadzu GC-2010 Plus with a FID detector (Dodecane as a GC internal standard). The reaction products were confirmed by GC-MS as well as by comparing

the retention times of standard substances in GC traces. The column chromatography using silica gel with petroleum ether/ethyl acetate as eluent was preferentially employed to isolate the product from the organic phase.

### Typical procedure for aerobic oxidation of alcohols to carboxylic acids

The oxidation reaction was carried out in a 25 mL round bottomed flask equipped with a condenser. Benzyl alcohol (5 mmol) and AC (0.6 g) were added and the mixture was stirred at 130 °C under O<sub>2</sub> atmosphere for a given period of time. After the completion of the reaction, the temperature was cooled to 80 °C and ethyl alcohol (10 mL) was added into the mixture for an hour until the product was completely dissolved. Then filtration was conducted to separate the solid catalyst, and the obtain residue was washed by ethyl alcohol to completely extract the organic compound. The ethyl alcohol extract mixtures were collected together and analysed by using Agilent GC-MS 7890 and Shimadzu GC-2010 Plus with a FID detector (Dodecane as a GC internal standard). The reaction products were confirmed by GC-MS as well as by comparing the retention times of standard substances in GC traces. The

product was purified by the column chromatography using silica gel with petroleum ether/ethyl acetate as eluent.

*Note:* The non-powdered activated carbons were ground and sieved to obtain 120–140 mesh powders and all the activated carbon catalysts were dried at 100 °C for 2 h before use.

## RESULTS AND DISCUSSION

In the research of our carbon-based catalysts, we incidentally found that commercial AC could catalyse the oxidation of benzyl alcohol to benzaldehyde without any treatment. In order to rule out the contingency, ACs from different producers were investigated (Table 1), and benzyl alcohol conversions from 6.4%–36.4% were obtained whereas the blank experiment only gave 1.5% conversion. This demonstrated that all the

ACs possessed catalytic activities for this oxidation reaction, but there were great differences in catalytic activity. It was found that powdery ACs exhibited higher catalytic performance than the preformed ACs. We speculated that the reason for this was that the forming process and the binder used had an adverse effect on catalytic activity. From the micro-perspective, the activity differences of AC could be ascribed to many things such as crystalline phase, elemental composition, pore system. Anyway, it was confirmed that commercial activated carbon without any modification displayed tangible catalytic activity for the transformation. It gave us a practical alternative for the alcohol oxidation catalyst since AC had advantages of excellent availability, low cost and environmental friendliness.

Table 1

Activated carbon screening for the oxidation of benzyl alcohol to aldehyde <sup>a</sup>

Entry	Activated carbon	Conv. of benzyl alcohol (%) <sup>b</sup>	Selec. (%) <sup>c</sup>		
			Benzaldehyde	Benzoic acid	Others
1	C <sub>1</sub>	36.4	96.7	1.8	1.5
2	C <sub>2</sub>	27.5	94.3	2.2	3.5
3	C <sub>3</sub>	10.5	98.7	n.d	1.3
4	C <sub>4</sub>	24.9	95.8	n.d	4.2
5	C <sub>5</sub>	17.8	95.3	n.d	4.7
6	C <sub>6</sub>	11.6	90.2	6.8	3.0
7	C <sub>7</sub>	7.1	95.4	n.d	4.6
8	C <sub>8</sub>	8.7	87.4	5.5	7.1
9	C <sub>9</sub>	10.8	98.3	n.d	1.7
10	C <sub>10</sub>	7.5	96.2	2.6	1.2
11	C <sub>11</sub>	6.4	94.4	n.d	5.6
12	—	1.5	91.0	n.d	9.0

<sup>a</sup> Reaction conditions: benzyl alcohol (5 mmol), activated carbon (0.3g), 120 °C, 8h, open air.

<sup>b, c</sup> Determined by GC.

Among these ACs, C<sub>1</sub> exhibited the highest catalytic performance (Entry 1, Table 1), so C<sub>1</sub> was selected as the catalyst to further optimize the reaction conditions of benzyl alcohol oxidation to benzaldehyde. Firstly, the reaction was performed over C<sub>1</sub> under different solvents and solvent-free condition in air atmosphere (Entry 1–6, Table 2). The results displayed that the desired product could be formed in the presence/absence of solvent, and best yield was obtained under solvent-free condition (Entry 6, Table 2). In the next set of experiments, different reaction atmospheres were attempted. As

expected, O<sub>2</sub> gave the highest conversion of benzyl alcohol (Entry 8, Table 2). Next, we increased catalyst amount to promote the transformation; the conversion reached 91.4% in the dosage of 0.5g and benzyl alcohol almost converted completely by further extending reaction time. However, it can be found that the selectivity of the desired product aldehyde kept falling in O<sub>2</sub> atmosphere (Entry 8–11, Table 2). This was caused by the over-oxidation of benzyl alcohol to benzoic acid. Thus, the key issue was how to regulate reaction process to obtain desired product with high selectivity.

Table 2  
Optimization of reaction conditions for oxidation of benzyl alcohol to aldehyde on commercial activated carbon <sup>a</sup>

Entry	Reaction conditions	Conv. of benzyl alcohol (%) <sup>b</sup>	Selec. (%) <sup>c</sup>		
			Benzaldehyde	Benzoic acid	Others
1	Toluene/Air	4.9	91.0	n.d	9.0
2	DMF/Air	10.5	93.2	0.8	6.0
3	DMSO/Air	15.1	90.5	3.9	5.6
4	1,2-dichloroethane/Air	3.9	99.0	n.d	1.0
5	H <sub>2</sub> O/Air	5.3	96.7	0.5	2.8
6	Solvent-free/Air	36.4	96.7	1.8	1.5
7	Solvent-free/N <sub>2</sub>	18.9	97.1	1.0	1.9
8	Solvent-free/O <sub>2</sub>	63.7	83.0	15.6	1.4
9 <sup>d</sup>	Solvent-free/O <sub>2</sub>	79.2	78.5	16.0	5.5
10 <sup>e</sup>	Solvent-free/O <sub>2</sub>	91.4	77.4	23.6	n.d
11 <sup>f</sup>	Solvent-free/O <sub>2</sub>	99.5	73.5	24.1	2.4

<sup>a</sup> Reaction conditions: benzyl alcohol (5 mmol), solvent (5 g), C<sub>1</sub> (0.3g), 120 °C, 8h. <sup>b, c</sup> Determined by GC. <sup>d</sup> C<sub>1</sub> (0.4g). <sup>e</sup> C<sub>1</sub> (0.5g). <sup>f</sup> C<sub>1</sub> (0.5g), 12h.

In the exploration of the solvent, we found that 1, 2-dichloroethane gave the highest aldehyde selectivity although the conversion was very low. Inspired by this, we tried to conduct the oxidation of benzyl alcohol in 1, 2-dichloroethane for high selectivity of aldehyde, a good result was obtained

(Entry 1, Table 3). Then we optimized the amount of 1, 2-dichloroethane and reaction time. Finally, the 96% yield of benzaldehyde was gained (Entry 6, Table 3). This demonstrated that the introduction of 1, 2-dichloroethane could effectively improve the selectivity of aldehyde.

Table 3  
Effect of the amount of 1, 2-dichloroethane on the oxidation of benzyl alcohol <sup>a</sup>

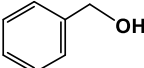
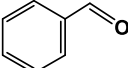
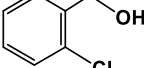
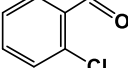
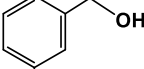
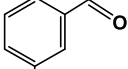
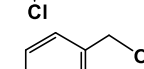
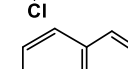
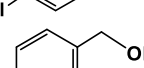
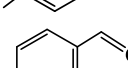
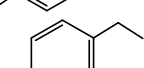
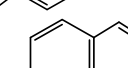
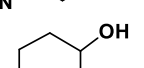
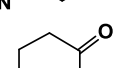
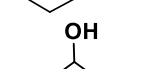
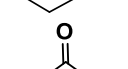
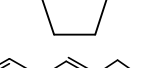
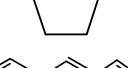

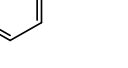
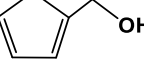
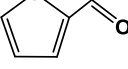
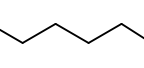
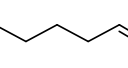
Entry	Reaction condition	Conv. of benzyl alcohol (%) <sup>b</sup>	Selec. (%)		
			Benzaldehyde	Benzoic acid	Others
1	1.6g <sup>c</sup> /120°C/12h	80.5	98.8	0.8	0.4
2	1.3g/120°C/12h	83.9	98.4	1.1	0.5
3	1.0g/120°C/12h	89.3	98.1	1.1	0.8
4	0.7g/120°C/12h	92.6	96.6	2.2	1.2
5	1.0g/130°C/12h	96.1	91.0	7.8	1.2
6	1.0g/120°C/16h	99.0	97.2	2.0	0.8

<sup>a</sup> Reaction conditions: C<sub>1</sub> (0.5g), benzyl alcohol (5 mmol), 1,2-dichloroethane, O<sub>2</sub> balloon. <sup>b</sup> Determined by GC. <sup>c</sup> Amounts of 1, 2-dichloroethane

Employing the optimum reaction condition, the universality of our procedure was explored using a wide range of structurally diverse alcohols. The results are summarized in Table 4. All ring substituted primary benzylic alcohols were oxidized to aldehyde with good to excellent yields. Alcohols with electron-donating substituents (-CH<sub>3</sub>) were oxidized more easily than alcohols with electron-withdrawing substituents (-Cl, -NO<sub>2</sub>) (Entry 2–6, Table 4). And, the reactivity of the regioisomer decreased in the order of para > meta > ortho isomer, which indicated the presence of a steric effect (Entry 2–4, Table 4). Secondary alicyclic saturated alcohols were also examined as

substrates, and the corresponding ketones were obtained in excellent yields (Entry 7 and 8, Table 4). In addition, the conversion rate of cinnamyl alcohol reached 100%, but the selectivity of cinnamaldehyde was low because the alkene bond was easily oxidized, leading to the formation of benzaldehyde (Entry 9, Table 4). For the same reason, furfuryl alcohol was degraded into some small molecules, so a very low selectivity of the desired furfural was given (Entry 10, Table 4). Finally, the oxidation of aliphatic alcohols was conducted. The results showed that it was difficult for aliphatic alcohols to oxidize in our protocol (Entry 10 and 11, Table 4).

Table 4  
 Selective oxidation of alcohols to aldehydes or ketones on C<sub>1</sub><sup>a</sup>

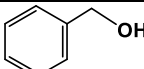
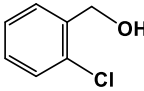
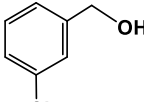
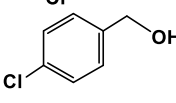
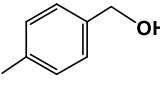
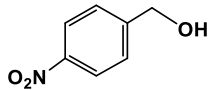
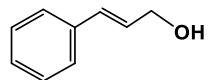
Entry	Substrate	Time/h	Product	Yields (%) <sup>b</sup>
1		16		96(90) <sup>c</sup>
2		20		90(82)
3		20		92(87)
4		20		95(88)
5		18		98(93)
6		20		87
7		16		99(93)
8		16		97
9		20		72
10		20		8
11		20		4
12		20		8

<sup>a</sup> Reaction conditions: C<sub>1</sub> (0.5g), alcohol (5 mmol), 1,2-dichloroethane (1g), O<sub>2</sub> balloon, 120 °C. <sup>b</sup> GC yields. <sup>c</sup> Isolated yields in parentheses.

Based on the above experimental results, alcohol could be oxidized more completely under solvent-free condition; we selected several alcohols with the relatively high reactivity to carry out the oxidation of alcohols into carboxylic acids under solvent-free condition. As shown in Table 5, various benzyl alcohols with different substituents could be oxidized

smoothly to the corresponding carboxylic acids with good yields under the optimized conditions (Entry 1–6, Table 5). For the oxidation of cinnamyl alcohol, only 32% of cinnamic acid was obtained, GC-MS analysis of the product mixture displayed that benzoic acid was the main byproduct due to the existence of oxidizable alkene bond.

Table 5  
Direct oxidation of alcohols to carboxylic acids by C<sub>1</sub><sup>a</sup>

Entry	Substrate	Time/h	Yields (%) <sup>b</sup>
1		24	94(89) <sup>c</sup>
2		28	91(83)
3		28	93(84)
4		28	95(89)
5		24	96(91)
6		24	88
7		24	32

<sup>a</sup> Reaction conditions: C<sub>1</sub> (0.6g), alcohol (5 mmol), O<sub>2</sub> balloon, 130 °C. <sup>b</sup> GC yields. <sup>c</sup> Isolated yields in parentheses.

At last, we evaluated the reusability of commercial activated carbon by the oxidation of benzyl alcohol to benzaldehyde as the probe reaction. Prior to reuse, the catalyst needed to be washed using ethanol twice under ultrasound irradiation. Figure 1 showed the reusability results of the C<sub>1</sub> activated carbon catalyst. A slight activity loss after five rounds was observed (96–92%), which demonstrated the excellent thermal and chemical stabilities of activated carbon catalyst.

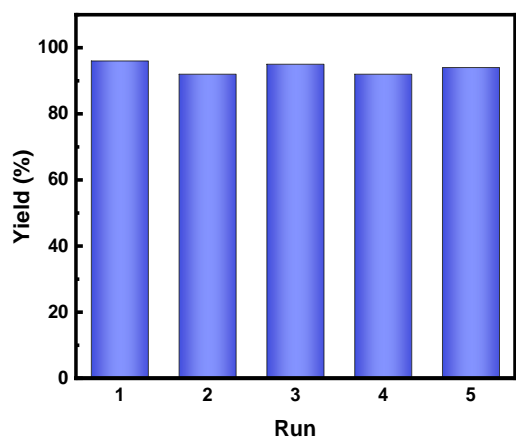


Fig. 1 – Reusability of the C<sub>1</sub> activated carbon catalyst.

## CONCLUSION

In this work, commercial activated carbon was employed to catalyse aerobic oxidation of alcohols; aldehydes/ketones and carboxylic acids were selectively furnished on activated carbon in the presence/absence of solvent. Benzylalcohols substituted with both electron-donating and electron-withdrawing along with aliphatic cyclic secondary alcohols were all competent substrates in our procedure. The activity test indicated that commercial activated carbon possessed tangible catalytic activity. Although the catalytic performance of commercial activated carbon was inferior to the reported metal catalyst, it had advantages of excellent availability, low cost, environmental benignity and good reproducibility. Our procedure provided an alternative for the selective aerobic oxidation of alcohol. More work is underway to further enhance catalytic performance and explore catalytic mechanism of activated carbon.

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