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Highly efficient carbon catalyzed aerobic selective oxidation of benzylic and allylic alcohols under transition-metal and heteroatom free conditions†

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The aerobic oxidation of benzylic and allylic alcohols has been realized with carbon material as the catalyst in the absence of transition-metal and heteroatoms. Under the optimized reaction conditions, aldehyde and acid can be selectively synthesized with up to 99% yields. The carbon catalyst can be easily recovered from the reaction mixture and can be reused for 5 runs without deactivation.

The aerobic oxidation of alcohols with high selectivity is a challenge with huge relevance from a fundamental point of view, and is also of great importance for industry due to the marketing value of the resulting compounds.1-4 This reaction has been performed by using heterogeneous catalysts⁵⁻¹⁰ and homogeneous metal complexes,11-16 as catalysts with O2 or peroxide as the oxidant. Usually, the most attractive way for alcohol oxidization is to use O2 as a terminal oxidant, where only H₂O is generated as a side-product. However, a persistent challenge of this transformation is the over-oxidation of aldehyde.8,17-20 It seems that due to the unavoidable formation of H₂O₂ as a byproduct in metal-containing catalyst systems, which can further react with aldehyde to produce acid and lead to selectivity loss. In order to address this problem, and also for the sake of sustainability and the rational use of resources, it would be highly desirable to develop nonmetallic catalysts for the oxidation of alcohols to the corresponding aldehydes and ketone.21,22

Catalysis by metal-free carbon has currently become a hot topic of much current interests in chemistry, since they have a number of advantages over the inorganic metal oxide materials (TiO₂, Fe₂O₃, SiO₂, and CeO₂ oxide supports^{8,23-26}), such as

higher chemical stability, larger surface area, and lower cost.27,28 Up to now, most reports of metal-free carbon materials are carbon-catalysts including graphene oxide,29-31 nitrogen-doped graphene^{32,33} and carbon nanotubes.^{19,34} Recently, the applying of graphene^{33,35-37} in the oxidation of alkane and alcohol has been made good progress.²² Wang and coworkers³⁷ reported that the multilayer graphene nano-sheets doped by Nheteroatoms can efficiently catalyze the aerobic selective oxidation of primary alcohols. The authors suggest that the oxygen molecules may be activated by the N-graphene to possibly form a sp² N– O_2 adduct transition state, which can oxidize alcohols to aldehydes. There is rare report about mesoporous and metal-free carbon material (not ordered grapheme and carbon nanotubes) without heteroatoms modification in the selective oxidation of alcohols. Herein, we first demonstrate new chemical function of transition metal-free carbon materials which can catalyze the controllable synthesis of aldehydes or acids from alcohols by altering the amount of base. As far as we know, it was also the first time using transition metal-free carbon materials to achieve chemoselective oxidation of alcohol to organic acid. This method offers a new alternative methodology for the development of sustainable catalysts.

In this work, the catalyst was prepared as following steps. First, RF gels (prepared by sol-gel polymerization of resorcinol and formaldehyde) were prepared through a hydrothermal method as the previous report,38 which is a sol-gel polymerization of resorcinol and formaldehyde with Na₂CO₃ as a catalyst. Next, RF gels were mixed together with base and were treated at 800 °C under nitrogen flow. Finally, the carbonized sample was washed by deionized water, and the carbon material was obtained. Several carbon materials were prepared with this method by varying the types and amount of bases. The RF gels itself was carbonized at 800 °C and was denoted as RF-HT-C-0 (RF: RF gels prepared by sol-gel polymerization of resorcinol and formaldehyde; HT: hydrothermal treatment; C: carbonization via thermal treatment). The carbon materials being treated by a mass ratio of 1 : 1 of RF and varied bases, *i.e.* KOH, NaOH, K₂CO₃ and Na₂CO₃, were denoted as RF-HT-C-1,

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RF-HT-C-2, RF-HT-C-3 and RF-HT-C-4, respectively. RF-HT-C-5 and RF-HT-C-6 were obtained by varying the mass ratio of RF and KOH to 1:0.25 and 1:1.25.

The structures of the carbon materials were characterized by SEM, BET, XPS and XRD. The morphology and structure of these as-made carbon catalyst samples were studied by SEM analysis. As shown in Fig. 1, the samples activated by different bases exhibit different porous structure after carbonization. BET characterization further indicates that the porosity of carbon material is well related to their surface areas as showed in Table 1. The surface area of RF-HT-C-0 was only 220.5 $m^2 g^{-1}$, which was un-activated by any base. The surface areas of other catalysts such as RF-HT-C-1, RF-HT-C-2, RF-HT-C-3, RF-HT-C-4, and RF-HT-C-5 were 1220.9, 408.1, 841.8, 407.7 and 582.0 m² g^{-1} , respectively. Moreover, no regular structures were observed in RF-HT-C-0, RF-HT-C-3 and RF-HT-C-4. The bonding configurations of C and O atoms in these carbon materials were further studied by XPS. As shown in Table S1 and Fig. S1,[†] C_{1s} peaks in the XPS spectra of the RF-HT-C-1 to RF-HT-C-5 samples can be fitted into one peak centered at 284.7 \pm 0.1 eV, indicating that there are similar surface carbon species in these carbon materials samples. XRD diffraction patterns of the carbon materials are similar to the amorphous carbon materials, Fig. S2.[†] So the treatment of base only altered the porosity of the carbon materials without changing the crystal structure of carbon in the final samples.

In a preliminary experiment, benzyl alcohol (1 mmol) was treated with carbon materials (100 mg) with KOH as cocatalyst at 100 $^{\circ}$ C in toluene for 12 h in a sealed vessel using molecular



Fig. 1 SEM images of the carbon materials: (a) RF-HT-C-0, (b) RF-HT-C-1, (c) RF-HT-C-2, (d) RF-HT-C-3, (e) RF-HT-C-4 and (f) RF-HT-C-5.

Table 1	Properties	of the	typical	carbon	catal	vsts
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Catalysts	$S_{\rm BET}/{ m m}^2~{ m g}^{-1}$	Pore volume/ cm ³ g ⁻¹	Pore size/nm
RF-HT-C-0	220.5	0.044	4.85
RF-HT-C-1	1220.9	0.15	3.44
RF-HT-C-2	408.1	0.29	4.36
RF-HT-C-3	841.8	0.12	3.78
RF-HT-C-4	407.7	0.08	2.66
RF-HT-C-5	582.0	0.10	3.61

oxygen as an oxidant. As summarized in Table 2, the catalytic performance of the carbon materials was studied under various conditions. First, different kinds of catalysts were explored and it was clear that the selectivities of all catalysts were similar with

 Table 2
 Catalytic performance of the different conditions for benzyl alcohol aerobic oxidation^a

ÇO2	н	ÇH₂OF	1	сно
	carbon,C	D_2	carbon, O ₂	
	 2 mmol bas 	se	0.2 mmol ba	ise
Entry	Catalyst	Base/mmol	Yield ^b /%	Selectivity ^b /%
1	RF-HT-C-0/100	KOH/0.2	38	96
2	RF-HT-C-1/100	KOH/0.2	95	95
3	RF-HT-C-2/100	KOH/0.2	85	93
4	RF-HT-C-3/100	KOH/0.2	76	91
5	RF-HT-C-4/100	KOH/0.2	72	95
6	RF-HT-C-5/100	KOH/0.2	45	93
7	RF-HT-C-6/100	KOH/0.2	96	97
8	RF-HT-C-1/20	KOH/0.2	67	90
9	RF-HT-C-1/50	KOH/0.2	80	93
10	RF-HT-C-1/200	KOH/0.2	96	97
11 ^c	RF-HT-C-1/100	KOH/0.2	81	92
12^d	RF-HT-C-1/100	KOH/0.2	14	54
13^e	RF-HT-C-1/100	KOH/0.2	54	85
14	RF-HT-C-1/100	_	10	96
15	_	KOH/0.2	36	90
16	RF-HT-C-1/100	KOH/0.05	60	98
17	RF-HT-C-1/100	KOH/0.1	92	96
18^{f}	RF-HT-C-1/100	KOH/0.5	60	62
19 ^f	RF-HT-C-1/100	KOH/1	21	24
20^{f}	RF-HT-C-1/100	KOH/2	0	0
21^g	RF-HT-C-1/100	KOH/0.2	80	93
22^h	RF-HT-C-1/100	KOH/0.2	96	97
23^i	RF-HT-C-1/100	KOH/0.2	74	90
24^{j}	RF-HT-C-1/100	KOH/0.2	90	93
25^k	RF-HT-C-1/100	KOH/0.2	93	91
26^l	AC/100	KOH/0.2	25	94

^{*a*} 1 mmol benzyl alcohol, 100 mg catalyst, 0.2 mmol KOH, 2 mL toluene, 1 atm oxygen, 100 °C, 12 h. ^{*b*} Determined by GRF-HT-C-FID using biphenyl as external standard. The main byproduct was the corresponding carboxylic acid. ^{*c*} Xylene was used as solvent. ^{*d*} Water was used as solvent. ^{*e*} Dioxane was used as solvent. ^{*f*} The byproduct was benzoic acid. The isolated yield of benzoic acid was 92% when 0.2 equiv., of KOH was used. ^{*g*} Reacted at 80 °C. ^{*h*} Reacted at 120 °C. ^{*i*} Reacted for 6 h. ^{*j*} Reacted for 24 h. ^{*k*} Reacted at 80 °C for 24 h. ^{*l*} Commercial sample, Vulcan XRF-HT-C-72 S_{BET} = 235 m² g⁻¹.

different conversions. Low activity of catalyst RF-HT-C-0 was observed for the selective oxidation of benzvl alcohol to the corresponding benzaldehyde. The yield of benzaldehyde was only 38% (entry 1). The yields were 95%, 85%, 76%, 72% and 45% if RF-HT-C-1, RF-HT-C-2, RF-HT-C-3, RF-HT-C-4 and RF-HT-C-5 were used as catalysts, respectively (entries 2-7). Therefore, the treatment of the carbon material with bases can improve the catalytic performance significantly. From results given in Table 2, RF-HT-C-1 and RF-HT-C-6 had similar catalytic activity, but RF-HT-C-1 was the more suitable catalyst than RF-HT-C-6 because it needs fewer bases during the treatment. Next, the influence of the catalyst loading, solvent, temperature, and reaction time were also studied. Clearly, low yield would be obtained if the catalyst loading less than 100 mg, therefore, the suitable quantity of catalyst should be 100 mg (entries 8-10, 15). Among the solvents tested, good yield was observed in xylene (81%) and the selectivity remained high (92%) (entry 11). If water was employed as solvent, 26% conversion was obtained but the selectivity was only 54% because benzoic acid as the byproduct was formed (entry 12). So the presence of large amount of water might deactivate the catalyst. The conversion of benzyl alcohol was 64% and the selectivity of benzaldehyde was 85% if using dioxane as solvent (entry 13). Moreover, the reaction temperature and reaction time optimization indicated that the reaction could be conducted completely at 100 °C for 12 h. Finally, the amount of cocatalyst was investigated and it had a remarkable effect on the reaction. The yield was only 10% if no base was added, but it was increased remarkably when 10% mmol or 20% mmol KOH was added (entries 1, 14 and 17). If the base amount reached to 50% mmol or higher, i.e. 100% mmol, the yield and selectivity of benzaldehyde decreased, and a large amount of benzoic acid was produced (entries 18, 19). Noteworthy when the quantity of KOH reached 200% mmol, no benzaldehyde was generated, because the benzyl alcohol was totally transformed to benzoic acid, and 92% isolated yield of benzoic acid was achieved (entry 20). The above results showed that aldehydes and acids can be synthesized from the corresponding alcohols with high selectivity by adjusting the amount of base. Under similar operating conditions, the catalytic performance of RF-HT-C-1 was found to be much better than the commercial carbon material such as activated carbon (entry 26). The lower yield using commercial AC as catalyst might be caused by the adsorption of base.

After the realization of benzyl alcohol oxidation to benzaldehyde catalyzed by carbon material, we applied RF-HT-C-1 in the selective oxidation of a series of benzylic alcohols having substitutions ranging from primary and secondary alcohols under the optimized reaction conditions for aldehyde synthesis (Table 3). For all these derivatives, good conversions and selectivities could be easily obtained. In order to compare the electronic effect of different substituents, benzyl alcohol derivatives contain electron-donating groups and electronwithdrawing groups were tested. The reaction results indicated that CH_3 or OCH_3 group had a beneficial effect on the reaction, but F, Cl and NO_2 were negative (entries 1–14). Benzyl alcohols with *p*-CH₃ and *p*-OCH₃ groups had conversions of around 99% and 98% at 100 °C after 12 h, respectively. On the

Table 3	Ovidation of	fvarious	alcohols	to	aldehydes
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Entry	Substrate	Time/h	Con /%	Vield ^b /%
		11110/11	0011.770	
1	ÓH	12	99	90
2	ОН	12	92	80
3	ОН	12	97	85
4	МеО	12	98	89
5	ОН	12	88	76
6	MeO	12	92	81
7	F ОН	18	92	84
8	ОН	18	82	73
9	F	18	85	76
10	СІОН	18	93	70
11	ОН	18	80	68
12	СІОН	18	88	71
13	Вг	24	85	71
14	O ₂ N OH	24	75	60
15 ^c	ОН	24	72	49
16 ^c	OH	24	89	78
17 ^d	С ОН	24	93	83
18^d	NOH	24	90	77

 a 1 mmol alcohol, 100 mg RF-HT-C-1, 0.2 mmol KOH, 2 mL toluene, 1 atm O₂, 100 °C, 12 h. b Determined by GRF-HT-C-FID using biphenyl as external standard. c Reacted at 120 °C. d ¹H NMR yield.

other hand, benzyl alcohols with *p*-F, *p*-Cl, *p*-Br and *p*-NO₂ groups gave conversions of 92%, 93%, 85% and 75%, respectively. Consequently, cinnamyl alcohol and 1-phenylethyl

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alcohol could also be oxidized to the desired products with 49% and 78% yields, respectively (entries 15–16). This catalyst was also active for the oxidation of heteroaromatic benzylic alcohols. For example, the yields to the desired products were 83% and 77% when using furan-2-ylmethanol and pyridin-3-ylmethanol as starting materials (entries 17–18). However, no oxidation reaction occurs if using aliphatic alcohols, such as 1-hexanol and 2-hexanol as starting materials.

Following, we further investigated the selective oxidation of alcohols to carboxylic acids. To the best of our knowledge, to date, the metal-free carbon material has not been reported as an efficient catalyst in the synthesis of carboxylic acid via alcohol oxidation. The range of suitable substrates for this catalytic system was investigated, and the results were listed in Table 4. RF-HT-C-1 can effectively catalyze the oxidation of aromatic alcohols to the corresponding carboxylic acids. Benzyl alcohol was quantitatively converted to benzoic acid at 100 °C for 12 h (entry 1). Moreover, benzyl alcohols with electron-donating groups such as p-CH₃ and p-OCH₃ can be easily converted to the corresponding acids with 85-99% isolated yields (entries 2-5). For benzylic alcohols with F, Cl and Br substituents, 80-98% yields of the corresponding carboxylic acids can be obtained (entries 6–10). For the oxidation of *p*-isopropyl benzyl alcohol, 91% yield of the corresponding carboxylic acid was realized (entry 11). Finally, 90% yield of p-trifluoromethyl benzoic acid was also achieved via the oxidation of p-trifluoromethyl benzyl alcohol (entry 12). In addition, the position of the substituent also affected the reactivity of benzyl alcohol derivatives. If taking methyl benzyl alcohol as an example, the reactivity decreased in the order of p-CH₃, m-CH₃ and o-CH₃ (entries 2-4), and the same reactivity order could be found in chlorobenzyl alcohol (entries 7-9). These results indicated that the substituent at the orthoposition might hinder its reactivity. In addition, furan-2ylmethanol and pyridin-3-ylmethanol can be oxidized into the corresponding acids with 85% and 95% yields (entries 13-14). The above reaction results show that RF-HT-C-1 is effective for the oxidation of alcohols to corresponding carboxylic acids.

In order to check the reusability of the carbon material catalyst, five reaction runs were carried out using benzyl alcohol oxidation as model reaction. After each reaction the catalyst was separated by filtration, washed with water and ethanol for three times, and dried at 80 °C for 6 h. The recovered catalyst was used in the recycling study under the same reaction conditions. It can be seen that the yield of benzaldehyde at the 5^{th} run was almost the same as the fresh catalyst (Table 5), indicating that RF-HT-C-1 is stable and recyclable.

In summary, carbon material has been demonstrated to be an active catalyst in the selective oxidation of various alcohols to aldehydes or acids by molecular oxygen under metal- and heteroatom-free conditions. These reactions were found to proceed under relatively mild conditions and the controlled synthesis of the desired product (aldehyde or acid) was realized. Moreover, catalyst recovery was found to be both convenient and effective using simple filtration techniques. To the best of our knowledge, these results constitute the first example to facilitate synthetically useful transformations *via* alcohol oxidation.

Table 4	Oxidation	of various	alcohols t	to carbox	vlic acids ^a
	Oxidation	or various	acconots	to carbox	yuc acius

Entry	Substrate	Yield ^b /%
1	ОН	92%
2	ОН	99%
3	ОН	83%
4	ОН	85%
5	Н₃СО	96%
6	Р	85%
7	СІ	98%
8	СІ	80%
9	CIOH	92%
10	Br	92%
11	ОН	91%
12	F F OH	90%
13	С. С	85%
14	NOH	95% ^c

 a 1 mmol alcohol, 100 mg RF-HT-C-1, 2 mmol KOH, 2 mL toluene, 1 atm O₂, 100 °C, 12 h. b Isolated yield, extracted by ethyl acetate after neutralizing the mixture with diluted hydrochloric acid. c NMR yield.

Table 5 Reusability test of RF-HT-C-1 for benzaldehyde synthesis^a

Entry	Run	Yield ^b /%
1	First	95
2	Second	91
3	Third	93
4	Fourth	90
5	Fifth	91

 a 1 mmol benzyl alcohol, 100 mg RF-HT-C-1, 0.2 mmol KOH, 2 mL toluene, 1 atm O_2 100 $^\circ \rm C,$ 12 h. b GC yield.

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Notes and references

- 1 T. Mallat and A. Baiker, Chem. Rev., 2004, 104, 3037.
- 2 T. Tsukuda, H. Tsunoyama and H. Sakurai, *Chem.-Asian J.*, 2011, **6**, 736.
- 3 F. Shi, M. K. Tse and M. Beller, Chem.-Asian J., 2007, 2, 411.
- 4 R. A. Sheldon, I. Arends and A. Dijksman, *Catal. Today*, 2000, **57**, 157.
- 5 Y. Chen, H. Wang, C.-J. Liu, Z. Zeng, H. Zhang, C. Zhou, X. Jia and Y. Yang, *J. Catal.*, 2012, **289**, 105.
- 6 Y. Hao, G.-P. Hao, D.-C. Guo, C.-Z. Guo, W.-C. Li, M.-R. Li and A.-H. Lu, *ChemCatChem*, 2012, 4, 1595.
- 7 A. Tanaka, K. Hashimoto and H. Kominami, J. Am. Chem. Soc., 2012, 134, 14526.
- 8 E. J. Garcia-Suarez, M. Tristany, A. B. Garcia, V. Colliere and K. Philippot, *Microporous Mesoporous Mater.*, 2012, **153**, 155.
- 9 B. S. Takale, M. Bao and Y. Yamamoto, *Org. Biomol. Chem.*, 2014, **12**, 2005. and publications cited therein.
- N. Asao, N. Hatakeyama, Menggenbateer, T. Minato, E. Ito, M. Hara, Y. Kim, Y. Yamamoto, M. Chen, W. Zhang and A. Inoue, *Chem. Commun.*, 2012, 48, 4540.
- 11 J. Zhu, P. C. Wang and M. Lu, Appl. Catal., A, 2014, 477, 125.
- 12 G. Chen, S. Wu, H. Liu, H. Jiang and Y. Li, *Green Chem.*, 2013, 15, 230.
- 13 A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *ACS Catal.*, 2011, 1, 48.
- 14 H. Liu, Y. Liu, Y. Li and H. Jiang, *J. Phys. Chem. C*, 2010, **114**, 13362.
- 15 M. J. Schultz, S. S. Hamilton, D. R. Jensen and M. S. Sigman, J. Org. Chem., 2005, **70**, 3343.
- 16 S. K. Hanson, R. Wu and L. A. P. Silks, *Org. Lett.*, 2011, **13**, 1908.
- 17 H. Li, R. Liu, S. Lian, H. Huang and Z. Kang, *Nanoscale*, 2013, 5, 3289.
- 18 K. Liu, T. Chen, Z. Hou, Y. Wang and L. Dai, *Catal. Lett.*, 2014, **144**, 314.

- 19 J. Luo, F. Peng, H. Yu and H. Wang, *Chem. Eng. J.*, 2012, **204**, 98.
- 20 X. Yu, Y. Huo, J. Yang, S. Chang, Y. Ma and W. Huang, *Appl. Surf. Sci.*, 2013, **280**, 450.
- 21 M. B. Lauber and S. S. Stahl, ACS Catal., 2013, 3, 2612.
- 22 K. Chen, P. Zhang, Y. Wang and H. Li, *Green Chem.*, 2014, 16, 2344.
- 23 S. Higashimoto, R. Shirai, Y. Osano, M. Azuma, H. Ohue, Y. Sakata and H. Kobayashi, *J. Catal.*, 2014, **311**, 137.
- 24 A. Mariana Balu, A. Pineda, K. Yoshida, J. Manuel Campelo,
 P. L. Gai, R. Luque and A. Angel Romero, *Chem. Commun.*, 2010, 46, 7825.
- 25 S. F. J. Hackett, A. F. Lee, A. D. Newman, K. Wilson, M. H. Gass, I. Harvey and R. M. Brydson, *Angew. Chem.*, *Int. Ed.*, 2007, 46, 8593.
- 26 Z. Li, R. M. Richards and C. Kuebel, J. Am. Chem. Soc., 2009, 237, 816.
- 27 Y. Kuang, N. M. Islam, Y. Nabae, T. Hayakawa and M.-a. Kakimoto, *Angew. Chem., Int. Ed.*, 2010, **49**, 436.
- 28 D. Haag and H. H. Kung, Top. Catal., 2014, 57, 762.
- 29 H. Yu, X. Wang, Y. Zhu, G. Zhuang, X. Zhong and J.-G. Wang, *Chem. Phys. Lett.*, 2013, **583**, 146.
- 30 L. Geng, S. Wu, Y. Zou, M. Jia, W. Zhang, W. Yan and G. Liu, J. Colloid Interface Sci., 2014, 421, 71.
- 31 D. W. Boukhvalov, D. R. Dreyer, C. W. Bielawski and Y.-W. Son, *ChemCatChem*, 2012, 4, 1844.
- 32 J. Vijaya Sundar and V. Subramanian, *Org. Lett.*, 2013, **15**, 5920.
- 33 A. Dhakshinamoorthy, A. Primo, P. Concepcion, M. Alvaro and H. Garcia, *Chem.-Eur. J.*, 2013, **19**, 7547.
- 34 J. Luo, H. Yu, H. Wang and F. Peng, *Chem. Eng. J.*, 2014, 240, 434.
- 35 D. R. Dreyer, H.-P. Jia and C. W. Bielawski, *Angew. Chem., Int. Ed.*, 2010, **49**, 6813.
- 36 H. P. Mungse, S. Verma, N. Kumar, B. Sain and O. P. Khatri, J. Mater. Chem., 2012, 22, 5427.
- 37 J. Long, X. Xie, J. Xu, L. Chen and X. Wang, *ACS Catal.*, 2012, 2, 622.
- 38 H. Yang, X. Cui, Y. Deng and F. Shi, *J. Mater. Chem.*, 2012, 22, 21852.